



## SM358

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# Additional Exercises for Book 3

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## Contents

Exercises	1
Solutions	11

*This set of exercises relates to Book 3 of SM358 and can be used for further practice and for revision purposes. To gain maximum benefit, it is important to attempt each question for yourself before looking up the solution.*

## Exercises

### Topic 1 — Spherical harmonics

**Exercise 1.1** (a) Show that the function

$$f(\theta) = A \cos \theta,$$

where  $A$  is a constant, is simultaneously an eigenfunction of

$$\hat{L}^2 = -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

and

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}.$$

Find the corresponding eigenvalue in each case.

(b) Find a value of  $A$  that ensures that  $f(\theta)$  is a normalized spherical harmonic,  $Y_{lm}(\theta, \phi)$ . What are the values of  $l$  and  $m$  in this case?

You may use the standard integral

$$\int_0^\pi \cos^2 \theta \sin \theta \, d\theta = \frac{2}{3}.$$

**Exercise 1.2** At time  $t = 0$ , a system is described by the normalized wave function

$$\Psi(\mathbf{r}, 0) = f(r) \left[ \frac{3}{5} Y_{1,1}(\theta, \phi) + \frac{4}{5} Y_{1,0}(\theta, \phi) \right].$$

- (a) Show that the angular part of the wave function is normalized.
- (b) If the square of the orbital angular momentum is measured at  $t = 0$  in the state  $\Psi(\mathbf{r}, 0)$ , what is the probability of getting the value  $2\hbar^2$ ?
- (c) If the  $z$ -component of the orbital angular momentum is measured at  $t = 0$  in the state  $\Psi(\mathbf{r}, 0)$ , what is the probability of getting the value  $\hbar$ ?

## Topic 2 — Total angular momentum

**Exercise 2.1** Show explicitly that

$$|A\rangle = \sqrt{\frac{1}{3}} Y_{1,0} |\uparrow\rangle - \sqrt{\frac{2}{3}} Y_{1,1} |\downarrow\rangle$$

and

$$|B\rangle = \sqrt{\frac{2}{3}} Y_{1,0} |\uparrow\rangle + \sqrt{\frac{1}{3}} Y_{1,1} |\downarrow\rangle$$

are both normalized and are orthogonal to one another.

**Exercise 2.2** Show that

$$|B\rangle = \sqrt{\frac{2}{3}} Y_{1,0} |\uparrow\rangle + \sqrt{\frac{1}{3}} Y_{1,1} |\downarrow\rangle$$

is an eigenvector of  $\hat{J}_z$ , and find the corresponding eigenvalue.

**Exercise 2.3** (a) The identity

$$\hat{J}^2 = (\hat{\mathbf{L}} + \hat{\mathbf{S}}) \cdot (\hat{\mathbf{L}} + \hat{\mathbf{S}}) = \hat{\mathbf{L}}^2 + 2\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} + \hat{\mathbf{S}}^2$$

can be rearranged to give

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{1}{2} (\hat{J}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2).$$

Use this result to show that the kets

$$|l, j, m_j\rangle = |1, \frac{1}{2}, \frac{1}{2}\rangle \quad \text{and} \quad |l, j, m_j\rangle = |1, \frac{3}{2}, \frac{1}{2}\rangle,$$

which represent states of a spin- $\frac{1}{2}$  particle, are eigenvectors of the operator  $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$  for such a particle, and find the corresponding eigenvalues.

(b) Why, in the physics of atomic hydrogen, is it significant that these eigenvectors have different eigenvalues of  $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ ?

## Topic 3 — Hydrogen atom

**Exercise 3.1** Allowing for different values of the spin magnetic quantum number  $m_s$ , determine how many degenerate states in the Coulomb model of a hydrogen atom have energy  $-E_R/16$ , where  $E_R$  is the Rydberg energy. Explain how you obtained your answer from the restrictions that apply to the quantum numbers  $l$ ,  $m$  and  $m_s$ .

**Exercise 3.2** In the Coulomb model of a hydrogen atom, the energy eigenfunctions are written as  $\psi_{nlm}(r, \theta, \phi)$ , where  $n$  is the principal quantum number,  $l$  is the orbital angular momentum quantum number and  $m$  is the magnetic quantum number. State the mathematical and physical reasons why the only allowed values of  $m$ ,  $l$  and  $n$  are integers.

**Exercise 3.3** In the Coulomb model of a hydrogen atom, radial functions with  $l = n - 1$  take the form

$$R_{nl}(r) = C r^{n-1} e^{-r/na_0},$$

where  $C$  is a normalization constant and  $a_0$  is the Bohr radius. Show that the radial probability density for a state with  $l = n - 1$  has its maximum value at  $r = n^2 a_0$ . Use your answer to estimate the typical size of a hydrogen atom with  $l = 99$  and  $n = 100$  and calculate how much energy would be needed to ionize the atom in this state. The Bohr radius is  $a_0 = 5.29 \times 10^{-11}$  m and the Rydberg energy is  $E_R = 13.6$  eV.

**Exercise 3.4** The energy eigenfunction in the 2s state of a hydrogen atom takes the form

$$\psi_{2,0,0}(r, \theta, \phi) = \frac{1}{\sqrt{4\pi}} R_{2,0}(r),$$

where the radial function is

$$R_{2,0}(r) = \frac{1}{(2a_0)^{3/2}} \left( 2 - \frac{r}{a_0} \right) e^{-r/2a_0},$$

and  $a_0$  is the Bohr radius. Show that the expectation value of  $r$  is  $6a_0$ .

You may use the standard integral

$$\int_0^\infty r^n e^{-r/a} dr = n! a^{n+1},$$

for any positive constant  $a$  and non-negative integer  $n$ .

**Exercise 3.5** (a) Find the expectation value of  $1/r^3$  in the hydrogen atom state described by the normalized energy eigenfunction

$$\psi_{2,1,0}(r, \theta, \phi) = \frac{1}{\sqrt{4\pi}} \left( \frac{1}{2a_0} \right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \cos \theta,$$

where  $a_0$  is the Bohr radius.

You may use the standard integrals

$$\int_0^\pi \cos^2 \theta \sin \theta d\theta = \frac{2}{3} \quad \text{and} \quad \int_0^\infty r^n e^{-r/a} dr = n! a^{n+1},$$

where  $a$  is a positive constant and  $n$  is a non-negative integer.

(b) Can you suggest a physical context in which evaluating the expectation value of  $1/r^3$  in a hydrogen atom energy eigenstate would be useful?

**Exercise 3.6** This question concerns the hydrogen atom energy eigenstate

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi) = R_{nl}(r) \Theta_{lm}(\theta) e^{im\phi}.$$

- (a) Show that the expectation and uncertainty of  $r$  are independent of the magnetic quantum number  $m$  in the state  $\psi_{nlm}$ .
- (b) Show that the probability density at any given point is independent of the azimuthal angle  $\phi$  in the state  $\psi_{nlm}$ .
- (c) Show that the radial probability density at a given radial coordinate is independent of  $m$ ,  $\theta$  and  $\phi$  in the state  $\psi_{nlm}$ .

**Exercise 3.7** This question concerns the ground state of a hydrogen atom, for which the normalized energy eigenfunction is

$$\psi_{1,0,0}(r, \theta, \phi) = \left( \frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0},$$

where  $a_0$  is the Bohr radius. Given that the operator for the square of the momentum of a particle is

$$\hat{p}^2 = -\hbar^2 \nabla^2 = \hbar^2 \left[ -\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{\hat{L}^2}{r^2} \right],$$

show that

$$\hat{p}^2 \psi_{1,0,0}(r, \theta, \phi) = \frac{\hbar^2}{a_0^2} \left( \frac{2a_0}{r} - 1 \right) \psi_{1,0,0}(r, \theta, \phi),$$

and hence find the expectation value of  $p^2$  in the ground state of a hydrogen atom.

You may use the standard integral

$$\int_0^\infty r^n e^{-r/a} dr = n! a^{n+1},$$

for any positive constant,  $a$  and non-negative integer  $n$ .

## Topic 4 — Perturbation theory

**Exercise 4.1** A particle of mass  $m$  is in the one-dimensional infinite potential energy well

$$V(x) = \begin{cases} \lambda|x| & \text{for } -L/2 \leq x \leq L/2 \\ \infty & \text{elsewhere,} \end{cases}$$

where  $\lambda$  is a small constant.

Use first-order perturbation theory to estimate the lowest two energy eigenvalues for this system, taking as the unperturbed system the particle in an infinite square well with walls at  $x = \pm L/2$ .

You may use the integrals

$$\int_0^{\pi/2} u \cos^2 u \, du = \frac{\pi^2 - 4}{16} \quad \text{and} \quad \int_0^\pi u \sin^2 u \, du = \frac{\pi^2}{4}.$$

**Exercise 4.2** A particle of mass  $m$  is in the one-dimensional infinite potential energy well

$$V(x) = \begin{cases} \lambda & \text{for } 0 \leq |x| \leq w/2 \\ 0 & \text{for } w/2 \leq |x| \leq L/2 \\ \infty & \text{elsewhere,} \end{cases}$$

where  $\lambda$  is a small constant and  $0 < w \leq L$ . Use first-order perturbation theory to estimate the ground-state energy of this system.

You may use the standard indefinite integral

$$\int \cos^2 u \, du = \frac{u}{2} + \frac{1}{4} \sin(2u).$$

**Exercise 4.3** For the purposes of this question, suppose that the electrostatic potential energy of two point charges  $e$  and  $-e$ , separated by a distance  $r$ , is given by

$$V(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1 + e^{-r/\lambda}}{r},$$

where  $\lambda$  is a positive constant that is small compared to the Bohr radius,  $a_0$ . What consequences would such a deviation from Coulomb's law have for the ground-state energy of a hydrogen atom?

You can model the electron and proton in a hydrogen atom as point charges, and take the ground-state energy eigenfunction in the Coulomb model to be

$$\psi_{1,0,0}(r, \theta, \phi) = \left( \frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0}.$$

You may use the standard integral

$$\int_0^\infty r^n e^{-\alpha r} dr = \frac{n!}{\alpha^{n+1}},$$

where  $\alpha$  is a positive constant and  $n$  is a non-negative integer.

**Exercise 4.4** The relativistic perturbation to the kinetic energy of a particle of mass  $m$  can be approximated by the expression

$$\delta\hat{H} = -\frac{(\hat{p}^2)^2}{8m^3c^2}.$$

Find the corresponding first-order correction to the ground-state energy of a hydrogen atom. You may use the following facts:

- The unperturbed ground-state energy eigenfunction is

$$\psi_{1,0,0}(r, \theta, \phi) = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0},$$

where  $a_0$  is the Bohr radius.

- Because  $\hat{p}^2$  is Hermitian, we have  $\langle\psi|\hat{p}^4|\psi\rangle = \langle\hat{p}^2\psi|\hat{p}^2\psi\rangle$ .
- $\hat{p}^2 e^{-r/a_0} = \frac{\hbar^2}{a_0^2} \left(\frac{2a_0}{r} - 1\right) e^{-r/a_0}$ .

You may use the standard integral

$$\int_0^\infty r^n e^{-r/a} dr = n! a^{n+1}$$

for any positive constant,  $a$  and non-negative integer  $n$ .

*The following exercise asks you to derive a useful result that is not discussed elsewhere in the course. It is included here because some of the methods used in the derivation are similar to those used to obtain the formula for the first-order correction in perturbation theory.*

**Exercise 4.5** Suppose that a Hamiltonian operator  $\hat{H}_\lambda$  depends on a parameter  $\lambda$ , which may take different values in different systems. For example, the Hamiltonian operator for a harmonic oscillator

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} C x^2,$$

contains the constants  $m$  and  $C$ , which can be regarded as parameters. Given the Hamiltonian operator  $\hat{H}_\lambda$ , the corresponding energy eigenvalues and normalized eigenvectors also depend on the parameter  $\lambda$ , and may be denoted by  $E_{n,\lambda}$  and  $|\psi_{n,\lambda}\rangle$ , so we have

$$\hat{H}_\lambda |\psi_{n,\lambda}\rangle = E_{n,\lambda} |\psi_{n,\lambda}\rangle.$$

In this question, you are asked to show that

$$\frac{\partial E_{n,\lambda}}{\partial \lambda} = \left\langle \psi_{n,\lambda} \left| \frac{\partial \hat{H}_\lambda}{\partial \lambda} \right| \psi_{n,\lambda} \right\rangle,$$

a result known as the Hellmann–Feynman theorem. Show first that

$$\frac{\partial E_{n,\lambda}}{\partial \lambda} = \left\langle \frac{\partial \psi_{n,\lambda}}{\partial \lambda} \left| \hat{H}_\lambda \right| \psi_{n,\lambda} \right\rangle + \left\langle \psi_{n,\lambda} \left| \frac{\partial \hat{H}_\lambda}{\partial \lambda} \right| \psi_{n,\lambda} \right\rangle + \left\langle \psi_{n,\lambda} \left| \hat{H}_\lambda \right| \frac{\partial \psi_{n,\lambda}}{\partial \lambda} \right\rangle.$$

Then use the fact that  $\hat{H}_\lambda$  is Hermitian, and the normalization condition  $\langle \psi_{n,\lambda} | \psi_{n,\lambda} \rangle = 1$  to show that

$$\left\langle \frac{\partial \psi_{n,\lambda}}{\partial \lambda} \left| \hat{H}_\lambda \right| \psi_{n,\lambda} \right\rangle + \left\langle \psi_{n,\lambda} \left| \hat{H}_\lambda \right| \frac{\partial \psi_{n,\lambda}}{\partial \lambda} \right\rangle = 0,$$

and hence complete the proof.

*Having derived the Hellmann–Feynman theorem, it may be interesting to see it in use.*

**Exercise 4.6** (a) The Hamiltonian operator for a harmonic oscillator is

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}Cx^2,$$

where  $C$  is the force constant and  $m$  is the mass. This has energy eigenvalues

$$E_n = (n + \frac{1}{2})\hbar\sqrt{\frac{C}{m}}$$

with corresponding eigenfunctions  $\psi_n(x)$ , where  $n$  is the quantum number. Treating  $C$  as a parameter, use the Hellmann–Feynman theorem to show that the expectation value of the potential energy in the eigenstate  $\psi_n$  is equal to half the total energy  $E_n$ .

(b) The Hamiltonian operator in the Coulomb model of a hydrogen atom is

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r},$$

where  $e$  is the electron charge and  $\mu$  is the reduced mass. This has energy eigenvalues

$$E_n = -\frac{e^4}{(4\pi\epsilon_0)^2} \frac{\mu}{2\hbar^2} \frac{1}{n^2},$$

with corresponding eigenfunctions  $\psi_{nlm}(r, \theta, \phi)$ . Treating the electron charge  $e$  as a parameter, use the Hellmann–Feynman theorem to show that the expectation value of the potential energy in the eigenstate  $\psi_{nlm}$  is equal to twice the total energy  $E_n$ .

## Topic 5 — Variational method

**Exercise 5.1** A one-dimensional system consists of a particle of mass  $m$ , subject to the finite square well potential energy function

$$V(x) = \begin{cases} -V_0 & \text{for } 0 \leq x \leq L \\ 0 & \text{elsewhere.} \end{cases}$$

(a) Use the trial function  $\phi_t = e^{-\alpha x^2/2}$ , where  $\alpha$  is a positive adjustable parameter, to show that

$$E_t \equiv \frac{\langle \phi_t | \hat{H} | \phi_t \rangle}{\langle \phi_t | \phi_t \rangle} = \frac{\hbar^2}{4m} \alpha - \frac{V_0}{\sqrt{\pi}} \int_0^{\sqrt{\alpha}L} e^{-u^2} du,$$

where

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

is the Hamiltonian operator of the system.

You may use the standard integrals

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}} \quad \text{and} \quad \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = \frac{\sqrt{\pi}}{2\alpha^{3/2}},$$

where  $\alpha$  is a positive constant.

(b) Show that, when  $\alpha$  is very small and positive,  $E_t < 0$ , and hence show that the ground-state energy eigenfunction in any finite square well has an energy below the top of the well, no matter how shallow or narrow the well may be.

You may use the fact that

$$\int_0^x e^{-u^2} du \simeq x \quad \text{when } x \ll 1.$$

**Exercise 5.2** A particle of mass  $m$ , in three dimensions, has the Hamiltonian operator

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \frac{1}{2}m\omega_0^2 r^2,$$

where  $\omega_0$  is a positive constant and  $r$  is the particle's radial coordinate in spherical coordinates. Obtain a variational estimate for the ground-state energy of this system, using the trial function

$$\phi_t(r) = e^{-r/a},$$

where  $a$  is a positive adjustable parameter.

You may use the fact that, when  $\nabla^2$  acts on any function  $f(r)$  that is independent of  $\theta$  and  $\phi$ , it gives

$$\nabla^2 f(r) = \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{df}{dr} \right).$$

You may use the standard integral

$$\int_0^\infty r^n e^{-r/a} dr = n! a^{n+1}.$$

for any positive constant  $a$  and non-negative integer  $n$ .

**Exercise 5.3** Repeat the calculation for the Hamiltonian operator given in Exercise 5.2, but using the trial function

$$\phi_t(r) = e^{-r^2/2a^2}.$$

You may use the standard integrals

$$\int_0^\infty r^2 e^{-r^2/a^2} dr = \frac{\sqrt{\pi}}{4} a^3 \quad \text{and} \quad \int_0^\infty r^4 e^{-r^2/a^2} dr = \frac{3\sqrt{\pi}}{8} a^5,$$

where  $a$  is a positive constant.

## Topic 6 — Hydrogen-like systems

**Exercise 6.1** Calculate the scaled Bohr radius (in m) and the scaled Rydberg energy (in eV) for a muonic atom of  $^4\text{He}$ , which can be considered to be a bound state of a muon (of charge  $-e$  and mass  $207m_e$ ) and a helium-4 nucleus (of charge  $2e$  and mass  $7360m_e$ ), where  $e$  and  $m_e$  are the magnitude of the charge and the mass of an electron.

You may take the Rydberg energy and Bohr radius to be  $E_R = 13.6 \text{ eV}$  and  $a_0 = 5.29 \times 10^{-11} \text{ m}$ . You may also take the reduced mass of a hydrogen atom to be the same as the mass of an electron.

**Exercise 6.2** Find the scaled Bohr radius and the energy of the ground state of positronium, a bound state of an electron and its antiparticle, the positron. In a hydrogen atom, the Bohr radius and Rydberg energy are  $5.29 \times 10^{-11} \text{ m}$  and  $13.6 \text{ eV}$ . You may take the reduced mass of a hydrogen atom to be the same as the mass of an electron.

## Topic 7 — Relativistic hydrogen atom

**Exercise 7.1** The Coulomb model of a hydrogen atom treats the electron and proton as point charges that interact only via the Coulomb force. List the additional effects that occur in real hydrogen atoms and give rise to fine and hyperfine structure in the hydrogen atom spectrum.

**Exercise 7.2** (a) In the absence of the spin-orbit interaction, the hydrogen atom has 8 degenerate quantum states with  $n = 2$ . Specify these states in terms of their  $n$ ,  $l$ ,  $m$  and  $m_s$  quantum numbers.

(b) When the spin-orbit interaction is included, the  $n = 2$  states are classified by the quantum numbers  $n$ ,  $l$ ,  $j$  and  $m_j$ . Specify the 8 hydrogen atom states with  $n = 2$  in terms of their  $n$ ,  $l$ ,  $j$  and  $m_j$  quantum numbers. Which of these states have the same energy according to relativistic quantum mechanics (which includes spin-orbit effects)?

**Exercise 7.3** In the first-order perturbation theory of the relativistic hydrogen atom, every unperturbed energy level is affected *either* by the spin–orbit interaction *or* by the Darwin term, but not by both. Explain why this is so.

**Exercise 7.4** (a) Express  $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$  in terms of  $\hat{L}^2$ ,  $\hat{S}^2$  and  $\hat{J}^2 = (\hat{\mathbf{L}} + \hat{\mathbf{S}})^2$ .

(b) Consider two quantum states,  $|A\rangle$  and  $|B\rangle$ , in a hydrogen atom, both labelled by the same values of  $n$  and  $l$ , with  $l > 0$ , but with  $j = l + \frac{1}{2}$  and  $j = l - \frac{1}{2}$ , respectively. Use your answer to part (a) to show that the first-order energy corrections for these states, due to the spin–orbit interaction, are in the ratio

$$\frac{E_A^{(1)}}{E_B^{(1)}} = -\frac{l}{l+1}.$$

## Topic 8 — Many-electron atoms

**Exercise 8.1** Explain why, in the central-field approximation for a many-electron atom, energy eigenfunctions can be labelled by the quantum numbers  $n$ ,  $l$  and  $m$ , just as in a hydrogen atom.

In the Coulomb model of a hydrogen atom, the energy levels depend on the principal quantum number,  $n$ , but are independent of  $l$ . Why does this not apply in many-electron atoms? For a given value of  $n$ , does the energy increase or decrease with  $l$ ? Give physical reasons for your answer.

**Exercise 8.2** (a) List all the atomic shells for  $n = 1, 2, 3$  and  $4$ , and give their capacities.

(b) Given that the energy ordering of atomic shells is:  $1s, 2s, 2p, 3s, 3p, 4s, 3d, \dots$ , write down the ground-state configuration of a silicon atom ( $Z = 14$ ) and an iron atom ( $Z = 26$ ).

## Topic 9 — Atomic terms and levels

**Exercise 9.1** An atom has a pair of valence electrons in open shells with  $(l_1 = 1, s_1 = \frac{1}{2})$  and  $(l_2 = 3, s_2 = \frac{1}{2})$ . Specify the atomic terms that arise from this configuration in terms of the values of their  $L$  and  $S$  quantum numbers, and give an appropriate spectroscopic symbol for each term.

**Exercise 9.2** The excited states of a helium atom have one electron in the lowest energy atomic orbital and the other electron in a higher energy atomic orbital. In these excited states, triplet states have lower energies than singlet states. Explain why this is so, using an argument based on first-order perturbation theory. Your argument need not contain any equations, but should emphasize the role of identical particles and electron–electron repulsion.

## Topic 10 — Molecules

**Exercise 10.1** A beryllium atom, Be, has atomic number  $Z = 4$ . Write down the ground-state electronic configuration of a diatomic beryllium molecule,  $\text{Be}_2$ , and determine its formal bond order. You may assume that molecular orbitals of  $\text{Be}_2$  are in order of increasing energy:  $1\sigma_g, 1\sigma_u, 2\sigma_g, 2\sigma_u, \dots$ , where  $1\sigma_g$  and  $2\sigma_g$  are bonding orbitals and  $1\sigma_u$  and  $2\sigma_u$  are antibonding orbitals. Would you expect a  $\text{Be}_2$  molecule to have a high dissociation energy?

**Exercise 10.2** (a) What is the physical basis of the Born–Oppenheimer approximation? How does the assumption of the Born–Oppenheimer approximation allow the time-independent Schrödinger equation for a molecule to be simplified?

(b) What is an energy curve for an electronic state of a diatomic molecule and how does the assumption of the Born–Oppenheimer approximation allow such a curve to be constructed?



**Exercise 10.3** (a) Consider a hydrogen molecule in the Born–Oppenheimer approximation. Suppose (for the purposes of this question) that the ground-state electronic energy eigenvalue is given by

$$E_{\text{el}}(R) = \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{5} \frac{a^4}{R^5} - \frac{2}{R} \right),$$

where  $a$  is a constant length and  $R$  is the proton–proton separation. Write down an expression for the total static energy of the molecule in this electronic ground state.

(b) Use your answer to part (a) to determine the equilibrium separation of the protons and the spectroscopic dissociation energy for a hydrogen molecule in its electronic ground state.

**Exercise 10.4** In the LCAO approximation, the ground-state energy eigenfunction for a hydrogen molecule ion has the form

$$\psi_1(\mathbf{r}) = C (\phi_{1s}^A(\mathbf{r}) + \phi_{1s}^B(\mathbf{r})),$$

where  $\phi_{1s}^A$  and  $\phi_{1s}^B$  are real-valued atomic orbitals centred on the two protons, A and B, and  $C$  is a normalization constant.

(a) Derive an expression for  $C$  in terms of the interatomic overlap integral  $\langle \phi_{1s}^A | \phi_{1s}^B \rangle$ .

(b) Explain why  $\psi_1(\mathbf{r})$  corresponds to a bonding molecular orbital, while a function of the form

$$\psi_2(\mathbf{r}) = D (\phi_{1s}^A(\mathbf{r}) - \phi_{1s}^B(\mathbf{r})),$$

where  $D$  is a suitable constant, does not.

## Topic 11 — Solids

**Exercise 11.1** State Bloch’s theorem for the state of an electron in an infinite crystalline solid. Show that it implies that the electron probability density is the same at all lattice points in the crystal.

**Exercise 11.2** Consider the function

$$u(\mathbf{r}) = \sum_i \phi(\mathbf{r} - \mathbf{R}_i) e^{i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{r})},$$

where each  $\mathbf{R}_i$  is a lattice vector, the sum is over the lattice vectors in an infinite crystal and  $\mathbf{k}$  is a real constant vector.

(a) Show that  $u(\mathbf{r})$  has the periodicity of the lattice.

(b) Hence show that the function

$$\psi(\mathbf{r}) = \sum_i \phi(\mathbf{r} - \mathbf{R}_i) e^{i\mathbf{k} \cdot \mathbf{R}_i},$$

where each  $\mathbf{R}_i$  is a lattice vector and the sum is over the lattice vectors in an infinite crystal, satisfies Bloch’s theorem.

**Exercise 11.3** A donor atom in its lowest energy configuration in germanium has an extra bound electron compared to a germanium atom. How much energy must be supplied to the donor atom for the extra electron to become unbound? You may treat the donor atom plus its additional electron as a hydrogen-like atom with an effective atomic number  $Z = 1$  and assume that the effective mass of an electron in the conduction band of germanium is  $m_e^* = 0.12m_e$ . The relative permittivity of germanium is  $\epsilon = 15.8$  (making the Coulomb force between charges in silicon smaller than that in empty space by a factor  $1/15.8$ ).

**Exercise 11.4** Explain why the electrical conductivity of a typical metal decreases with increasing temperature, while the electrical conductivity of a typical pure semiconductor increases with increasing temperature.

## Topic 12 — Interaction of light and matter

**Exercise 12.1** (a) Which types of radiative transition have transition probabilities that can be predicted directly using first-order time-dependent perturbation theory?

(b) If stationary states are timeless and unchanging in quantum mechanics, how is it possible for a transition to occur spontaneously between two stationary states in an isolated atom?

**Exercise 12.2** For monochromatic light polarized in the  $z$ -direction, the electric dipole approximation introduces a time-dependent perturbation

$$V(t) = f(t)z = f(t)r \cos \theta,$$

which is independent of the azimuthal angle,  $\phi$ . Show that, according to the results of first-order time-dependent perturbation theory, such light will cause no radiative transitions between two hydrogen atom states that have different values of the magnetic quantum number,  $m$ .

**Exercise 12.3** For monochromatic light polarized in the  $x$ -direction, the electric dipole approximation introduces a time-dependent perturbation

$$V(t) = f(t)x = f(t)r \sin \theta \cos \phi,$$

Show that, according to the results of first-order time-dependent perturbation theory, such light will cause no radiative transitions between two hydrogen atom states that have the *same* value of the magnetic quantum number,  $m$ .

**Exercise 12.4** (a) Define the three different types of radiative transition.

(b) The following equation applies to atoms in equilibrium with radiation:

$$B_{12}u(\omega_{21})N_1 = B_{21}u(\omega_{21})N_2 + A_{21}N_2$$

where  $B_{12}$ ,  $B_{21}$  and  $A_{21}$  are constants,  $N_1$  and  $N_2$  are the numbers of atoms in quantum states 1 and 2, of energies  $E_1$  and  $E_2$  (with  $E_2 > E_1$ ),  $u(\omega)$  is the spectral energy density function and  $\omega_{21} = (E_2 - E_1)/\hbar$ .

Correlate the three terms in this equation with the three types of radiative transition defined in part (a).

# Solutions

## Topic 1 — Spherical harmonics

**Solution 1.1** (a) We have

$$\begin{aligned}
 \hat{L}^2 f(\theta) &= -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] A \cos \theta \\
 &= -A \hbar^2 \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d \cos \theta}{d\theta} \right) \\
 &= A \hbar^2 \frac{1}{\sin \theta} \frac{d}{d\theta} (\sin^2 \theta) \\
 &= A \hbar^2 \frac{1}{\sin \theta} \times 2 \sin \theta \cos \theta \\
 &= 2 \hbar^2 A \cos \theta,
 \end{aligned}$$

so  $f(\theta)$  is an eigenfunction of  $\hat{L}^2$  with eigenvalue  $2\hbar^2$ .

Also,

$$\begin{aligned}
 \hat{L}_z A \cos \theta &= -i\hbar \frac{\partial}{\partial \phi} A \cos \theta \\
 &= 0 \\
 &= 0 \times A \cos \theta,
 \end{aligned}$$

so  $f(\theta)$  is an eigenfunction of  $\hat{L}_z$  with eigenvalue 0.

(b) We require that

$$\begin{aligned}
 1 &= \int_0^{2\pi} \int_0^\pi |A|^2 \cos^2 \theta \sin \theta d\theta d\phi \\
 &= 2\pi |A|^2 \int_0^\pi \cos^2 \theta \sin \theta d\theta \\
 &= 2\pi |A|^2 \times \frac{2}{3} \\
 &= \frac{4}{3} \pi |A|^2,
 \end{aligned}$$

so we can choose  $A = \sqrt{3/4\pi}$ .

In general, the eigenvalues of  $\hat{L}^2$  and  $\hat{L}_z$  are  $l(l+1)\hbar^2$  and  $m\hbar$  respectively, so  $(\sqrt{3/4\pi}) \cos \theta$  is a normalized spherical harmonic,  $Y_{lm}$ , with quantum numbers  $l = 1$  and  $m = 0$ .

**Comments** (1) There is no problem with having an eigenvalue equal to zero. Whenever  $\hat{O}f(x) = 0$ , we can say that  $f(x)$  is an eigenfunction of  $\hat{O}$  with eigenvalue 0.

(2) Normalization of an angular function  $f(\theta, \phi)$  requires that

$$\int_0^{2\pi} \int_0^\pi |f(\theta, \phi)|^2 \sin \theta d\theta d\phi = 1.$$

Note that the integrand contains a factor  $\sin \theta$  and the limits are:  $0 \leq \theta \leq \pi$  and  $0 \leq \phi \leq 2\pi$ .

**Solution 1.2** (a) Using Dirac notation, the angular part of the wave function is

$$|\text{ang}\rangle = \frac{3}{5}|1, 1\rangle + \frac{4}{5}|1, 0\rangle,$$

so

$$\begin{aligned}
 \langle \text{ang} | \text{ang} \rangle &= \left[ \frac{3}{5}\langle 1, 1| + \frac{4}{5}\langle 1, 0| \right] \left[ \frac{3}{5}|1, 1\rangle + \frac{4}{5}|1, 0\rangle \right] \\
 &= \frac{9}{25}\langle 1, 1|1, 1\rangle + \frac{12}{25}\langle 1, 1|1, 0\rangle + \frac{12}{25}\langle 1, 0|1, 1\rangle + \frac{16}{25}\langle 1, 0|1, 0\rangle.
 \end{aligned}$$

The spherical harmonics are orthonormal so  $\langle 1, 1|1, 1\rangle = \langle 1, 0|1, 0\rangle = 1$  and  $\langle 1, 1|1, 0\rangle = \langle 1, 0|1, 1\rangle = 0$ .

Hence,

$$\langle \text{ang}|\text{ang}\rangle = \frac{9}{25} + \frac{16}{25} = 1,$$

as required.

(b) Both parts of the wave function contain spherical harmonics with  $l = 1$ . The wave function is therefore an eigenfunction of  $\hat{L}^2$  with eigenvalue  $1(1+1)\hbar^2 = 2\hbar^2$ . The probability of getting the value  $2\hbar^2$  in this state is equal to 1.

(c) The angular part of the wave function is normalized so we can use the coefficient rule to read off the probabilities of the possible values of  $L_z$ . The probability of getting the value  $\hbar$  is found by taking the square of the modulus of the coefficient of  $|1, 1\rangle$ , which gives  $|3/5|^2 = 9/25 = 0.36$ .

**Comments** (1) It is convenient to use the Dirac notation  $|l, m\rangle$  for  $Y_{lm}(\theta, \phi)$ , as it avoids the need to write down explicit integrals. Of course,

$$\langle l_1, m_1|l_2, m_2\rangle \equiv \int_0^{2\pi} \int_0^\pi Y_{l_1, m_1}^*(\theta, \phi) Y_{l_2, m_2}(\theta, \phi) \sin \theta \, d\theta \, d\phi.$$

(2) We are told that the whole wave function is normalized and we have shown that the angular part is normalized, so it follows that the radial part is also normalized:

$$\int_0^\infty |f(r)|^2 r^2 \, dr = 1.$$

Because of this, there is no need to worry about the radial part of the wave function when using the coefficient rule. Remember, the coefficient rule comes from the overlap rule. If the overlap rule were used directly to calculate the probability, the radial function would integrate out to give a factor of 1.

## Topic 2 — Total angular momentum

**Solution 2.1** Denoting  $Y_{lm}(\theta, \phi)$  by  $|l, m\rangle$ , we have

$$|A\rangle = \sqrt{\frac{1}{3}}|1, 0\rangle|\uparrow\rangle - \sqrt{\frac{2}{3}}|1, 1\rangle|\downarrow\rangle$$

$$|B\rangle = \sqrt{\frac{2}{3}}|1, 0\rangle|\uparrow\rangle + \sqrt{\frac{1}{3}}|1, 1\rangle|\downarrow\rangle.$$

The spherical harmonics are orthonormal, so we have

$$\langle l_1, m_1|l_2, m_2\rangle \equiv \int_0^{2\pi} \int_0^\pi Y_{l_1, m_1}^*(\theta, \phi) Y_{l_2, m_2}(\theta, \phi) \sin \theta \, d\theta \, d\phi = \delta_{l_2, l_1} \delta_{m_2, m_1}.$$

Hence,

$$\begin{aligned} \langle A|A\rangle &= \left( \sqrt{\frac{1}{3}}\langle 1, 0|\langle \uparrow| - \sqrt{\frac{2}{3}}\langle 1, 1|\langle \downarrow| \right) \left( \sqrt{\frac{1}{3}}|1, 0\rangle|\uparrow\rangle - \sqrt{\frac{2}{3}}|1, 1\rangle|\downarrow\rangle \right) \\ &= \frac{1}{3}\langle 1, 0|1, 0\rangle\langle \uparrow|\uparrow\rangle - \frac{\sqrt{2}}{3}\langle 1, 0|1, 1\rangle\langle \uparrow|\downarrow\rangle \\ &\quad - \frac{\sqrt{2}}{3}\langle 1, 1|1, 0\rangle\langle \downarrow|\uparrow\rangle + \frac{2}{3}\langle 1, 1|1, 1\rangle\langle \downarrow|\downarrow\rangle \\ &= \frac{1}{3}(1 \times 1) - \frac{\sqrt{2}}{3}(0 \times 0) - \frac{\sqrt{2}}{3}(0 \times 0) + \frac{2}{3}(1 \times 1) \\ &= 1. \end{aligned}$$

$$\begin{aligned} \langle B|B\rangle &= \left( \sqrt{\frac{2}{3}}\langle 1, 0|\langle \uparrow| + \sqrt{\frac{1}{3}}\langle 1, 1|\langle \downarrow| \right) \left( \sqrt{\frac{2}{3}}|1, 0\rangle|\uparrow\rangle + \sqrt{\frac{1}{3}}|1, 1\rangle|\downarrow\rangle \right) \\ &= \frac{2}{3}\langle 1, 0|1, 0\rangle\langle \uparrow|\uparrow\rangle + \frac{\sqrt{2}}{3}\langle 1, 0|1, 1\rangle\langle \uparrow|\downarrow\rangle \\ &\quad + \frac{\sqrt{2}}{3}\langle 1, 1|1, 0\rangle\langle \downarrow|\uparrow\rangle + \frac{1}{3}\langle 1, 1|1, 1\rangle\langle \downarrow|\downarrow\rangle \\ &= \frac{2}{3}(1 \times 1) + \frac{\sqrt{2}}{3}(0 \times 0) + \frac{\sqrt{2}}{3}(0 \times 0) + \frac{1}{3}(1 \times 1) \\ &= 1. \end{aligned}$$

So  $|A\rangle$  and  $|B\rangle$  are both normalized. Also

$$\begin{aligned}
\langle B|A\rangle &= \left(\sqrt{\frac{2}{3}}\langle 1,0|\uparrow\rangle + \sqrt{\frac{1}{3}}\langle 1,1|\downarrow\rangle\right)\left(\sqrt{\frac{1}{3}}|1,0\rangle|\uparrow\rangle - \sqrt{\frac{2}{3}}|1,1\rangle|\downarrow\rangle\right) \\
&= \frac{\sqrt{2}}{3}\langle 1,0|1,0\rangle\langle\uparrow|\uparrow\rangle - \frac{2}{3}\langle 1,0|1,1\rangle\langle\uparrow|\downarrow\rangle \\
&\quad + \frac{1}{3}\langle 1,1|1,0\rangle\langle\downarrow|\uparrow\rangle - \frac{\sqrt{2}}{3}\langle 1,1|1,1\rangle\langle\downarrow|\downarrow\rangle \\
&= \frac{\sqrt{2}}{3}(1 \times 1) - \frac{2}{3}(0 \times 0) + \frac{1}{3}(0 \times 0) - \frac{\sqrt{2}}{3}(1 \times 1) \\
&= 0.
\end{aligned}$$

Hence  $|A\rangle$  and  $|B\rangle$  are orthogonal.

**Comment** The space and spin parts of the total wave function act like they don't see one another. So, when we form the inner product of the total wave function and multiply out terms, the spin parts come together to produce their own inner products and the space parts do the same. The final answer is therefore a sum of terms, each of which is a product of two inner products – one involving spin states and one involving spatial states.

**Solution 2.2** With

$$|B\rangle = \left(\sqrt{\frac{2}{3}}Y_{1,0}|\uparrow\rangle + \sqrt{\frac{1}{3}}Y_{1,1}|\downarrow\rangle\right),$$

we have

$$\begin{aligned}
\hat{J}_z|B\rangle &= (\hat{L}_z + \hat{S}_z)|B\rangle \\
&= (\hat{L}_z + \hat{S}_z)\left(\sqrt{\frac{2}{3}}Y_{1,0}|\uparrow\rangle + \sqrt{\frac{1}{3}}Y_{1,1}|\downarrow\rangle\right) \\
&= \sqrt{\frac{2}{3}}(\hat{L}_zY_{1,0})|\uparrow\rangle + \sqrt{\frac{1}{3}}(\hat{L}_zY_{1,1})|\downarrow\rangle + \sqrt{\frac{2}{3}}Y_{1,0}(\hat{S}_z|\uparrow\rangle) + \sqrt{\frac{1}{3}}Y_{1,1}(\hat{S}_z|\downarrow\rangle) \\
&= 0\sqrt{\frac{2}{3}}Y_{1,0}|\uparrow\rangle + \hbar\sqrt{\frac{1}{3}}Y_{1,1}|\downarrow\rangle + \frac{1}{2}\hbar\sqrt{\frac{2}{3}}Y_{1,0}|\uparrow\rangle - \frac{1}{2}\hbar\sqrt{\frac{1}{3}}Y_{1,1}|\downarrow\rangle \\
&= \frac{1}{2}\hbar\left(\sqrt{\frac{2}{3}}Y_{1,0}|\uparrow\rangle + \sqrt{\frac{1}{3}}Y_{1,1}|\downarrow\rangle\right) \\
&= \frac{1}{2}\hbar|B\rangle,
\end{aligned}$$

so  $|B\rangle$  is an eigenvector of  $\hat{J}_z$  with eigenvalue  $\hbar/2$ .

**Comment** In an expression like  $(\hat{L}_z + \hat{S}_z)Y_{1,0}|\uparrow\rangle$ , we multiply out terms and remember that  $\hat{L}_z$  acts only on the spatial part ( $Y_{1,0}$  in this case), while  $\hat{S}_z$  acts only on the spin part ( $|\uparrow\rangle$  in this case). (To keep the notation compact we have omitted the angular arguments of the spherical harmonics, but we must not forget that these functions depend on the spatial coordinates  $\theta$  and  $\phi$ , and so are affected by the operator  $\hat{L}_z$ .)

**Solution 2.3** (a) For  $|l, j, m_j\rangle = |1, \frac{1}{2}, \frac{1}{2}\rangle$ , we have

$$\begin{aligned}
\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}|1, \frac{1}{2}, \frac{1}{2}\rangle &= \frac{1}{2}(\hat{J}^2 - \hat{L}^2 - \hat{S}^2)|1, \frac{1}{2}, \frac{1}{2}\rangle \\
&= \frac{1}{2}\left(\frac{1}{2}(\frac{1}{2} + 1) - 1(1 + 1) - \frac{1}{2}(\frac{1}{2} + 1)\right)\hbar^2|1, \frac{1}{2}, \frac{1}{2}\rangle \\
&= -\hbar^2|1, \frac{1}{2}, \frac{1}{2}\rangle.
\end{aligned}$$

For  $|l, j, m_j\rangle = |1, \frac{3}{2}, \frac{1}{2}\rangle$ , we have

$$\begin{aligned}
\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}|1, \frac{3}{2}, \frac{1}{2}\rangle &= \frac{1}{2}(\hat{J}^2 - \hat{L}^2 - \hat{S}^2)|1, \frac{3}{2}, \frac{1}{2}\rangle \\
&= \frac{1}{2}\left(\frac{3}{2}(\frac{3}{2} + 1) - 1(1 + 1) - \frac{1}{2}(\frac{1}{2} + 1)\right)\hbar^2|1, \frac{3}{2}, \frac{1}{2}\rangle \\
&= \frac{\hbar^2}{2}|1, \frac{3}{2}, \frac{1}{2}\rangle.
\end{aligned}$$

Hence  $|1, \frac{1}{2}, \frac{1}{2}\rangle$  and  $|1, \frac{3}{2}, \frac{1}{2}\rangle$  are eigenvectors of  $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$  with eigenvalues  $-\hbar^2$  and  $+\hbar^2/2$ , respectively.

(b) With spin-orbit coupling,  $|1, \frac{1}{2}, \frac{1}{2}\rangle$  and  $|1, \frac{3}{2}, \frac{1}{2}\rangle$  are atomic terms that develop from an unperturbed configuration in which the electron has  $l = 1$ . The spin-orbit interaction is proportional to  $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ , so the fact that these two eigenvectors have different eigenvalues of  $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$  leads to spin-orbit splitting in  $l = 1$  configurations.

**Comments** (1) By definition of the scalar product,

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \hat{L}_x \hat{S}_x + \hat{L}_y \hat{S}_y + \hat{L}_z \hat{S}_z,$$

but this is a very inconvenient expression for calculations because  $L_x$ ,  $L_y$  and  $L_z$  cannot all have definite non-zero values in the same state (and similarly for  $S_x$ ,  $S_y$  and  $S_z$ ). Nevertheless, the particular combination  $\hat{L}_x \hat{S}_x + \hat{L}_y \hat{S}_y + \hat{L}_z \hat{S}_z$  does have a definite value in any state with definite values of  $J^2$ ,  $L^2$  and  $S^2$ . We can find this value by using the identity given in the question.

(2) Note that  $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$  is the same as  $\hat{\mathbf{S}} \cdot \hat{\mathbf{L}}$  because each of the spatial operators  $\hat{L}_x$ ,  $\hat{L}_y$  and  $\hat{L}_z$  commutes with each of the spin operators  $\hat{S}_x$ ,  $\hat{S}_y$  and  $\hat{S}_z$ .

### Topic 3 — Hydrogen atom

**Solution 3.1** In the Coulomb model of a hydrogen atom, the energy levels are

$$E_n = -\frac{E_R}{n^2},$$

where  $n = 1, 2, 3, \dots$ , so the energy level  $-E_R/16$  has  $n = 4$ . The possible values of  $l$  are therefore 0, 1, 2 and 3.

For  $l = 0$ , the only allowed value of  $m$  is 0.

For  $l = 1$ , the allowed values of  $m$  are  $-1, 0$  and  $1$ .

For  $l = 2$ , the allowed values of  $m$  are  $-2, -1, 0, 1$  and  $2$ .

For  $l = 3$ , the allowed values of  $m$  are  $-3, -2, -1, 0, 1, 2$  and  $3$ .

This gives a total of  $1 + 3 + 5 + 7 = 16$  combinations of  $l$  and  $m$  for  $n = 4$ . For each of these combinations we can have  $m_s = \pm \frac{1}{2}$ , so there are  $16 \times 2 = 32$  degenerate states with energy  $-E_R/16$ .

**Comment** In the Coulomb model of a hydrogen atom,  $2n^2$  degenerate states are associated with the quantum number  $n$ . For  $n = 4$ , this gives  $2 \times 4^2 = 32$  states. This degree of degeneracy is lowered in the fine structure of a hydrogen atom (where energy levels depend on the  $n$ ,  $l$  and  $j$  quantum numbers) and in many-electron atoms, even in the central-field approximation.

**Solution 3.2** Using the method of separation of variables, the time-independent Schrödinger equation for the Coulomb model of a hydrogen atom can be split into separate equations for the  $r$ -,  $\theta$ - and  $\phi$ -dependencies, allowing us to write

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)\Theta_{lm}(\theta)e^{im\phi}.$$

The magnetic quantum number  $m$  must be an integer to give

$$e^{im(\phi+2\pi)} = e^{im\phi}.$$

This is needed to ensure that the energy eigenfunction is single-valued in the sense that

$$\psi_{nlm}(r, \theta, \phi + 2\pi) = \psi_{nlm}(r, \theta, \phi).$$

The function  $\Theta_{lm}(\theta)$  diverges as  $\theta \rightarrow 0$  and  $\theta \rightarrow \pi$  unless  $l$  is a positive integer greater than or equal to  $|m|$ . The function  $R_{nl}(r)$  diverges as  $r \rightarrow \infty$  unless  $n$  is an integer greater than  $l$ . These quantum numbers take integer values because it is assumed that the energy eigenfunction does not diverge anywhere.

**Comment** The requirement that the energy eigenfunction be single-valued is not entirely obvious. Certainly,  $|\psi(r, \theta, \phi)|^2$  must be single-valued because it represents a physically-measurable quantity – the probability density of finding a particle at a given place. The single-valued nature of  $\psi(r, \theta, \phi)$  is less clear-cut because an eigenfunction is not a measurable quantity. Nevertheless, once an overall constant phase factor has been chosen, quantum mechanics assumes that eigenfunctions and wave functions have definite values at each point in space, and this assumption gives the quantization condition for the magnetic quantum number  $m$ .

**Solution 3.3** Using the given form of radial function, the radial probability density is given by

$$r^2 R_{nl}^2(r) = r^2 \left( C r^{n-1} e^{-r/na_0} \right)^2 = C^2 r^{2n} e^{-2r/na_0}.$$

This is a maximum when

$$\begin{aligned} 0 &= \frac{d}{dr} \left( C^2 r^{2n} e^{-2r/na_0} \right) \\ &= C^2 \left( 2nr^{2n-1} - \frac{2r^{2n}}{na_0} \right) e^{-2r/na_0} \\ &= 2C^2 r^{2n-1} \left( n - \frac{r}{na_0} \right) e^{-2r/na_0}, \end{aligned}$$

which gives  $r = n^2 a_0$ .

For  $l = 99$  and  $n = 100$ , the typical size of a hydrogen atom is  $100^2 a_0 = 5.29 \times 10^{-7} \text{ m}$  (comparable with the wavelength of visible light). The energy of an atom in this state is  $-13.6 \text{ eV}/100^2 = -1.36 \text{ meV}$ , so the energy needed to ionize the atom is  $1.36 \text{ meV}$ .

**Comments** (1) Note that the radial probability density does NOT contain a factor of  $4\pi$ . This can be traced back to the fact that  $\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi)$ , where the spherical harmonic  $Y_{lm}(\theta, \phi)$  satisfies the normalization condition

$$\int_0^{2\pi} \int_0^\pi |Y_{lm}(\theta, \phi)|^2 \sin \theta \, d\theta \, d\phi = 1 \quad (\text{NOT } 4\pi).$$

(2) Hydrogen atoms in states with very high values of  $n$  (Rydberg states) have been prepared experimentally, but they are very easily ionized.

**Solution 3.4** The expectation value of  $r$  in the given 2s state is given by

$$\begin{aligned} \langle r \rangle &= \int_0^\infty R_{2,0}^*(r) r R_{2,0}(r) r^2 \, dr \\ &= \int_0^\infty R_{2,0}^2(r) r^3 \, dr \\ &= \frac{1}{(2a_0)^3} \int_0^\infty \left( 2 - \frac{r}{a_0} \right)^2 \left[ e^{-r/2a_0} \right]^2 r^3 \, dr \\ &= \frac{1}{(2a_0)^3} \int_0^\infty \left( 4r^3 - \frac{4r^4}{a_0} + \frac{r^5}{a_0^2} \right) e^{-r/a_0} \, dr. \end{aligned}$$

Using the standard integral given in the question and noting that  $3! = 6$ ,  $4! = 24$  and  $5! = 120$ , we obtain

$$\langle r \rangle = \frac{1}{8a_0^3} \left[ 4 \times 6a_0^4 - 4 \times \frac{24a_0^5}{a_0} + \frac{120a_0^6}{a_0^2} \right] = 6a_0.$$

**Comment** If we know the radial function  $R_{nl}(r)$ , the expectation value of any function of  $r$  can be found without doing any angular integration. In any state described by the radial function  $R_{nl}(r)$ , the expectation value of  $f(r)$  is given by

$$\langle f(r) \rangle = \int_0^\infty f(r) |R_{nl}(r)|^2 r^2 \, dr.$$

There is no factor of  $4\pi$  in this expression for reasons similar to those given in the preceding question.

**Solution 3.5** (a) We have

$$\begin{aligned}\left\langle \frac{1}{r^3} \right\rangle &= \int_0^{2\pi} \int_0^\pi \int_0^\infty \psi_{2,1,0}^*(r, \theta, \phi) \frac{1}{r^3} \psi_{2,1,0}(r, \theta, \phi) r^2 \sin \theta \, dr \, d\theta \, d\phi \\ &= \frac{1}{4\pi} \left( \frac{1}{2a_0} \right)^3 \frac{1}{a_0^2} \int_0^{2\pi} \int_0^\pi \int_0^\infty \frac{1}{r^3} \left[ r e^{-r/2a_0} \cos \theta \right]^2 r^2 \sin \theta \, dr \, d\theta \, d\phi \\ &= \frac{1}{4\pi} \left( \frac{1}{2a_0} \right)^3 \frac{1}{a_0^2} \int_0^{2\pi} d\phi \int_0^\pi \cos^2 \theta \sin \theta \, d\theta \int_0^\infty r e^{-r/a_0} \, dr.\end{aligned}$$

Using the standard integrals given in the question, we obtain

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{4\pi} \left( \frac{1}{2a_0} \right)^3 \frac{1}{a_0^2} \times 2\pi \times \frac{2}{3} \times 1! a_0^2 = \frac{1}{24a_0^3}.$$

(b) The spin-orbit interaction is proportional to  $1/r^3$ , so finding the expectation value of  $1/r^3$  in various states of a hydrogen atom is needed when calculating the first-order perturbation approximation for the spin-orbit splitting of hydrogen atom energy levels.

**Comments** (1) In this question the complete energy eigenfunction  $\psi_{nlm}(r, \theta, \phi)$  is given, but there is no obvious way of splitting this into a radial part and an angular part, each with appropriate normalization. We therefore resort to the sandwich rule for expectation values, using the complete energy eigenfunction and integrating over  $\theta$  and  $\phi$  as well as  $r$ .

(2) As in all volume integrals in spherical coordinates, we must use the volume element  $dV = r^2 \sin \theta \, dr \, d\theta \, d\phi$ .

**Solution 3.6** (a) The expectation value of  $r$  is given by

$$\begin{aligned}\langle r \rangle &= \int_0^{2\pi} \int_0^\pi \int_0^\infty r |R_{nl}(r) Y_{lm}(\theta, \phi)|^2 r^2 \sin \theta \, dr \, d\theta \, d\phi \\ &= \int_0^\infty r^3 |R_{nl}(r)|^2 \, dr \int_0^{2\pi} \int_0^\pi |Y_{lm}(\theta, \phi)|^2 \sin \theta \, d\theta \, d\phi \\ &= \int_0^\infty r^3 |R_{nl}(r)|^2 \, dr,\end{aligned}$$

because the spherical harmonics  $Y_{lm}$  are normalized. Similarly,

$$\langle r^2 \rangle = \int_0^\infty r^4 |R_{nl}(r)|^2 \, dr,$$

so  $\langle r \rangle$  and  $\Delta r = \sqrt{\langle r^2 \rangle - \langle r \rangle^2}$  are independent of  $m$ .

(b) The probability density at any given point is

$$\begin{aligned}|\psi_{nlm}(r, \theta, \phi)|^2 &= |R_{nl}(r) Y_{lm}(\theta, \phi)|^2 \\ &= |R_{nl}(r)|^2 |\Theta_{lm}(\theta)|^2 |e^{im\phi}|^2 \\ &= |R_{nl}(r)|^2 |\Theta_{lm}(\theta)|^2,\end{aligned}$$

which is independent of  $\phi$ .

(c) The radial probability density at any given radial coordinate is given by  $r^2 |R_{nl}(r)|^2$ , which is independent of  $m$ ,  $\theta$  and  $\phi$  (by definition, the radial probability density is a function only of  $r$ ).

**Comment** Part (a) could be answered more quickly using the general formula

$$\langle f(r) \rangle = \int_0^\infty f(r) |R_{nl}(r)|^2 r^2 \, dr,$$

but the above method shows explicitly why the dependence on  $m$  disappears when the angular integrations are carried out.



**Solution 3.7** We have

$$\begin{aligned}\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} e^{-r/a_0} \right) &= \frac{1}{r^2} \frac{d}{dr} \left( -\frac{r^2}{a_0} e^{-r/a_0} \right) \\ &= \frac{1}{r^2} \left( -\frac{2r}{a_0} + \frac{r^2}{a_0^2} \right) e^{-r/a_0}.\end{aligned}$$

The operator  $\hat{L}^2$  involves partial derivatives with respect to  $\theta$  and  $\phi$ , and so  $\hat{L}^2 e^{-r/a_0} = 0$ . Hence

$$\begin{aligned}\hat{p}^2 e^{-r/a_0} &= -\hbar^2 \nabla^2 e^{-r/a_0} \\ &= \frac{\hbar^2}{r^2} \left( \frac{2r}{a_0} - \frac{r^2}{a_0^2} \right) e^{-r/a_0} \\ &= \frac{\hbar^2}{a_0^2} \left( \frac{2a_0}{r} - 1 \right) e^{-r/a_0},\end{aligned}$$

and so

$$\hat{p}^2 \psi_{1,0,0} = \frac{\hbar^2}{a_0^2} \left( \frac{2a_0}{r} - 1 \right) \psi_{1,0,0}.$$

We therefore have

$$\begin{aligned}\langle p^2 \rangle &= \int_0^{2\pi} \int_0^\pi \int_0^\infty \psi_{1,0,0}^*(r, \theta, \phi) \hat{p}^2 \psi_{1,0,0}(r, \theta, \phi) r^2 \sin \theta \, dr \, d\theta \, d\phi \\ &= \int_0^{2\pi} \int_0^\pi \int_0^\infty \psi_{1,0,0}^*(r, \theta, \phi) \frac{\hbar^2}{a_0^2} \left( \frac{2a_0}{r} - 1 \right) \psi_{1,0,0}(r, \theta, \phi) r^2 \sin \theta \, dr \, d\theta \, d\phi \\ &= \frac{1}{\pi a_0^3} \int_0^{2\pi} \int_0^\pi \int_0^\infty e^{-r/a_0} \frac{\hbar^2}{a_0^2} \left( \frac{2a_0}{r} - 1 \right) e^{-r/a_0} r^2 \sin \theta \, dr \, d\theta \, d\phi \\ &= \frac{\hbar^2}{\pi a_0^5} 4\pi \int_0^\infty (2a_0 r - r^2) e^{-2r/a_0} \, dr \\ &= \frac{4\hbar^2}{a_0^5} \left[ 2a_0 \left( \frac{a_0}{2} \right)^2 - 2! \left( \frac{a_0}{2} \right)^3 \right] \\ &= \frac{4\hbar^2}{a_0^5} \left[ \frac{a_0^3}{2} - \frac{a_0^3}{4} \right] \\ &= \frac{\hbar^2}{a_0^2}.\end{aligned}$$

**Comment** The expectation value of any quantity has the units of that quantity. Recalling the de Broglie relation ( $\lambda_{dB} = h/p$ ), and noting that  $a_0$  is a length, it is easy to see that our answer has the correct dimensions for the expectation value of the square of momentum.

## Topic 4 — Perturbation theory

**Solution 4.1** Choose the unperturbed Hamiltonian to be that for a particle of mass  $m$  in the corresponding one-dimensional infinite square well, with

$$V^{(0)}(x) = \begin{cases} 0 & \text{for } -L/2 \leq x \leq L/2 \\ \infty & \text{elsewhere.} \end{cases}$$

In the ground state, the unperturbed energy eigenfunction is

$$\psi_1^{(0)}(x) = \sqrt{\frac{2}{L}} \cos\left(\frac{\pi x}{L}\right)$$

with eigenvalue  $E_1^{(0)} = \pi^2 \hbar^2 / 2mL^2$ . The perturbation is then

$$\delta\hat{H} = \begin{cases} \lambda|x| & \text{for } -L/2 \leq x \leq L/2 \\ 0 & \text{elsewhere.} \end{cases}$$

So first-order perturbation theory gives a first-order correction

$$E_1^{(1)} = \langle \psi_1^{(0)} | \delta\hat{H} | \psi_1^{(0)} \rangle.$$

Because the perturbation involves  $|x|$ , the integral we need to evaluate has an even integrand, and we can write

$$\begin{aligned} E_1^{(1)} &= 2 \times \frac{2}{L} \int_0^{L/2} \lambda x \cos^2 \left( \frac{\pi x}{L} \right) dx \\ &= \frac{4\lambda}{L} \int_0^{L/2} x \cos^2 \left( \frac{\pi x}{L} \right) dx. \end{aligned}$$

We change the variable of integration to  $u = (\pi x/L)$ . Then,  $x = (L/\pi)u$  and  $dx = (L/\pi)du$ . Also  $x = 0$  and  $x = L/2$  correspond to  $u = 0$  and  $u = \pi/2$ , so

$$\begin{aligned} E_1^{(1)} &= \frac{4\lambda}{L} \left( \frac{L}{\pi} \right)^2 \int_0^{\pi/2} u \cos^2 u \, du \\ &= \frac{4\lambda}{L} \left( \frac{L}{\pi} \right)^2 \times \frac{\pi^2 - 4}{16} \\ &= \frac{\lambda L}{4\pi^2} (\pi^2 - 4). \end{aligned}$$

The first-order approximation to the ground-state energy is

$$E_1 \simeq \frac{\pi^2 \hbar^2}{2mL^2} + \frac{\lambda L}{4\pi^2} (\pi^2 - 4).$$

In the first excited state, the unperturbed energy eigenfunction is

$$\psi_2^{(0)}(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{2\pi x}{L} \right)$$

with eigenvalue  $E_2^{(0)} = 4\pi^2 \hbar^2 / 2mL^2$ .

So first-order perturbation theory gives a first-order correction

$$\begin{aligned} E_2^{(1)} &= \langle \psi_2^{(0)} | \delta\hat{H} | \psi_2^{(0)} \rangle \\ &= 2 \times \frac{2}{L} \int_0^{L/2} \lambda x \sin^2 \left( \frac{2\pi x}{L} \right) dx \\ &= \frac{4\lambda}{L} \left( \frac{L}{2\pi} \right)^2 \int_0^{\pi} u \sin^2 u \, du \\ &= \frac{\lambda L}{4}. \end{aligned}$$

The first-order approximation to the energy of the first excited state is

$$E_2 \simeq \frac{4\pi^2 \hbar^2}{2mL^2} + \frac{\lambda L}{4}.$$

**Comment** For  $\lambda > 0$ , the energies of both states are *increased* by the perturbation, but the increase is smaller for the ground state than for the first-excited state. This is because the probability density in the ground state is largest around  $x = 0$ , where the perturbation is equal to zero. By contrast, the probability density has maxima away from  $x = 0$  in the first-excited state, where the perturbation is larger.

**Solution 4.2** Choose the unperturbed Hamiltonian to be that for a particle of mass  $m$  in the corresponding one-dimensional infinite square well, with

$$V^{(0)}(x) = \begin{cases} 0 & \text{for } -L/2 \leq x \leq L/2 \\ \infty & \text{elsewhere.} \end{cases}$$

In the ground state, the unperturbed energy eigenfunction is

$$\psi_1^{(0)}(x) = \sqrt{\frac{2}{L}} \cos\left(\frac{\pi x}{L}\right)$$

with eigenvalue  $E_1^{(0)} = \pi^2 \hbar^2 / 2mL^2$ . The perturbation is then

$$\delta\hat{H} = \begin{cases} \lambda & \text{for } -w/2 \leq x \leq w/2 \\ 0 & \text{elsewhere.} \end{cases}$$

The first-order correction to the ground-state energy is

$$\begin{aligned} E_1^{(1)} &= \langle \psi_1^{(0)} | \delta\hat{H} | \psi_1^{(0)} \rangle \\ &= \frac{2}{L} \int_{-w/2}^{w/2} \lambda \cos^2\left(\frac{\pi x}{L}\right) dx. \end{aligned}$$

Change the variable of integration to  $u = \pi x/L$ . Then  $dx = (L/\pi)du$ . Also,  $x = \pm w/2$  corresponds to  $u = \pm \pi w/2L$ . So

$$\begin{aligned} E_1^{(1)} &= \frac{2\lambda}{L} \frac{L}{\pi} \int_{-\pi w/2L}^{\pi w/2L} \cos^2 u \, du \\ &= \frac{2\lambda}{\pi} \left[ \frac{u}{2} + \frac{1}{4} \sin(2u) \right]_{-\pi w/2L}^{\pi w/2L} \\ &= \frac{4\lambda}{\pi} \left[ \frac{\pi w}{4L} + \frac{1}{4} \sin\left(\frac{\pi w}{L}\right) \right] \\ &= \lambda \left[ \frac{w}{L} + \frac{1}{\pi} \sin\left(\frac{\pi w}{L}\right) \right]. \end{aligned}$$

The ground-state energy of the system is therefore estimated to be

$$E_1 \simeq \frac{\pi^2 \hbar^2}{2mL^2} + \lambda \left[ \frac{w}{L} + \frac{1}{\pi} \sin\left(\frac{\pi w}{L}\right) \right].$$

**Comment** The correction tends to 0 as  $w \rightarrow 0$  and tends to  $\lambda$  as  $w \rightarrow L$ , as might be expected.

**Solution 4.3** We use perturbation theory with the potential energy function split into an unperturbed part  $V^{(0)}$  and a perturbation  $V^{(1)}$  where

$$V^{(0)}(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \quad \text{and} \quad \delta\hat{H} = -\frac{e^2}{4\pi\epsilon_0} \frac{e^{-r/\lambda}}{r}.$$

Perturbation theory then gives the first-order energy correction to be

$$\begin{aligned} E_1^{(1)} &= \langle \psi_{1,0,0} | \delta\hat{H} | \psi_{1,0,0} \rangle \\ &= \int_0^{2\pi} \int_0^\pi \int_0^\infty \psi_{1,0,0}^*(r, \theta, \phi) \delta\hat{H} \psi_{1,0,0}(r, \theta, \phi) r^2 \sin \theta \, dr \, d\theta \, d\phi \\ &= \frac{1}{\pi a_0^3} \left( -\frac{e^2}{4\pi\epsilon_0} \right) 4\pi \int_0^\infty e^{-r/a_0} \frac{e^{-r/\lambda}}{r} e^{-r/a_0} r^2 \, dr \\ &= -\frac{e^2}{\pi\epsilon_0 a_0^3} \int_0^\infty e^{-(2/a_0 + 1/\lambda)r} r \, dr. \end{aligned}$$

Using the standard integral given in the question, we obtain

$$\begin{aligned} E_1^{(1)} &= -\frac{e^2}{\pi\epsilon_0 a_0^3} \frac{1}{\left(\frac{2}{a_0} + \frac{1}{\lambda}\right)^2} \\ &= -\frac{e^2}{\pi\epsilon_0 a_0} \frac{\lambda^2}{(a_0 + 2\lambda)^2}. \end{aligned}$$

**Comment** Without the perturbation, the ground-state energy in the Coulomb model can be expressed as

$$E_1^{(0)} = -E_R = -\frac{e^2}{8\pi\epsilon_0 a_0},$$

so the ratio of the first-order correction to the unperturbed ground-state energy is

$$\frac{E_1^{(1)}}{E_1^{(0)}} = \frac{e^2}{\pi\epsilon_0 a_0} \frac{\lambda^2}{(a_0 + 2\lambda)^2} \times \frac{8\pi\epsilon_0 a_0}{e^2} = \frac{8\lambda^2}{(a_0 + 2\lambda)^2},$$

and for  $\lambda \ll a_0$ , this is approximately equal to  $8\lambda^2/a_0^2$ . So, if the ground-state energy agrees with the Coulomb model to one part in 1000,  $\lambda$  cannot be much larger than  $\sqrt{a_0^2/8000} \simeq 0.01a_0$ . This provides a check on the validity of Coulomb's law at short distances.

**Solution 4.4** A hydrogen atom is a two-particle system characterized by a reduced mass  $\mu$ . We can use the general formula for the relativistic perturbation to the kinetic energy (given in the question) with  $m$  replaced by  $\mu$ . The first-order correction is then

$$E_1^{(1)} = \langle \psi_{1,0,0} | \delta \hat{H} | \psi_{1,0,0} \rangle = -\frac{1}{8\mu^3 c^2} \langle \hat{p}^2 \psi_{1,0,0} | \hat{p}^2 \psi_{1,0,0} \rangle,$$

where  $\mu$  is the reduced mass for a hydrogen atom. Hence

$$\begin{aligned} E_1^{(1)} &= -\frac{1}{\pi a_0^3} \left( \frac{1}{8\mu^3 c^2} \right) \int_0^{2\pi} \int_0^\pi \int_0^\infty \left( \hat{p}^2 e^{-r/a_0} \right)^* \left( \hat{p}^2 e^{-r/a_0} \right) r^2 \sin \theta \, dr \, d\theta \, d\phi \\ &= -\frac{1}{\pi a_0^3} \left( \frac{1}{8\mu^3 c^2} \right) \int_0^{2\pi} \int_0^\pi \int_0^\infty \left( \frac{\hbar^2}{a_0^2} \left( \frac{2a_0}{r} - 1 \right) e^{-r/a_0} \right) \left( \frac{\hbar^2}{a_0^2} \left( \frac{2a_0}{r} - 1 \right) e^{-r/a_0} \right) r^2 \sin \theta \, dr \, d\theta \, d\phi \\ &= -\frac{1}{\pi a_0^3} \left( \frac{1}{8\mu^3 c^2} \right) \frac{\hbar^4}{a_0^4} 4\pi \int_0^\infty \left( 1 - \frac{4a_0}{r} + \frac{4a_0^2}{r^2} \right) e^{-2r/a_0} r^2 \, dr \\ &= -\frac{\hbar^4}{2\mu^3 c^2 a_0^7} \int_0^\infty (r^2 - 4a_0 r + 4a_0^2) e^{-2r/a_0} \, dr. \end{aligned}$$

So

$$\begin{aligned} E_1^{(1)} &= -\frac{\hbar^4}{2\mu^3 c^2 a_0^7} \left[ 2! \left( \frac{a_0}{2} \right)^3 - 4a_0 \left( \frac{a_0}{2} \right)^2 + 4a_0^2 \left( \frac{a_0}{2} \right) \right] \\ &= -\frac{\hbar^4}{2\mu^3 c^2 a_0^7} \left[ \frac{a_0^3}{4} - a_0^3 + 2a_0^3 \right] \\ &= -\frac{5\hbar^4}{8\mu^3 c^2 a_0^4} \\ &= -\frac{5}{2} \frac{E_R^2}{\mu c^2}, \end{aligned}$$

where  $E_R = \hbar^2/2\mu a_0^2$  is the Rydberg energy.

**Comments** (1) Because  $E_R$  and  $\mu c^2$  have the dimensions of energy, our final answer for the energy correction has the correct units of energy.

(2) The trick of using the Hermitian character of  $\hat{p}^2$  to write  $\langle \psi | \hat{p}^4 | \psi \rangle = \langle \hat{p}^2 \psi | \hat{p}^2 \psi \rangle$  is a useful one because it avoids having to work out the fourth derivative. In fact, the calculation of the fourth derivative is hazardous in this case because there is a singularity at the origin. This can be handled using an advanced mathematical technique beyond the scope of this course (the so-called Dirac delta function) but it is good to avoid such complications.

**Solution 4.5** We have

$$\hat{H}_\lambda |\psi_{n,\lambda}\rangle = E_{n,\lambda} |\psi_{n,\lambda}\rangle,$$

so

$$\langle \psi_{n,\lambda} | \hat{H}_\lambda | \psi_{n,\lambda} \rangle = E_{n,\lambda} \langle \psi_{n,\lambda} | \psi_{n,\lambda} \rangle = E_{n,\lambda},$$

because the eigenvectors are normalized.

Differentiating both sides gives

$$\frac{\partial E_{n,\lambda}}{\partial \lambda} = \left\langle \frac{\partial \psi_{n,\lambda}}{\partial \lambda} \middle| \hat{H}_\lambda \middle| \psi_{n,\lambda} \right\rangle + \left\langle \psi_{n,\lambda} \middle| \frac{\partial \hat{H}_\lambda}{\partial \lambda} \middle| \psi_{n,\lambda} \right\rangle + \left\langle \psi_{n,\lambda} \middle| \hat{H}_\lambda \middle| \frac{\partial \psi_{n,\lambda}}{\partial \lambda} \right\rangle.$$

Using the fact that  $\hat{H}_\lambda$  is Hermitian, and that  $\psi_{n,\lambda}$  is an eigenfunction of  $\hat{H}_\lambda$  with the real eigenvalue  $E_{n,\lambda}$ , we have

$$\left\langle \frac{\partial \psi_{n,\lambda}}{\partial \lambda} \middle| \hat{H}_\lambda \middle| \psi_{n,\lambda} \right\rangle = E_{n,\lambda} \left\langle \frac{\partial \psi_{n,\lambda}}{\partial \lambda} \middle| \psi_{n,\lambda} \right\rangle$$

and

$$\left\langle \psi_{n,\lambda} \middle| \hat{H}_\lambda \middle| \frac{\partial \psi_{n,\lambda}}{\partial \lambda} \right\rangle = \left\langle \hat{H}_\lambda \psi_{n,\lambda} \middle| \frac{\partial \psi_{n,\lambda}}{\partial \lambda} \right\rangle = E_{n,\lambda} \left\langle \psi_{n,\lambda} \middle| \frac{\partial \psi_{n,\lambda}}{\partial \lambda} \right\rangle.$$

Adding these two equations then gives

$$\begin{aligned} \left\langle \frac{\partial \psi_{n,\lambda}}{\partial \lambda} \middle| \hat{H}_\lambda \middle| \psi_{n,\lambda} \right\rangle + \left\langle \psi_{n,\lambda} \middle| \hat{H}_\lambda \middle| \frac{\partial \psi_{n,\lambda}}{\partial \lambda} \right\rangle &= E_{n,\lambda} \left( \left\langle \frac{\partial \psi_{n,\lambda}}{\partial \lambda} \middle| \psi_{n,\lambda} \right\rangle + \left\langle \psi_{n,\lambda} \middle| \frac{\partial \psi_{n,\lambda}}{\partial \lambda} \right\rangle \right) \\ &= E_{n,\lambda} \frac{\partial}{\partial \lambda} \langle \psi_{n,\lambda} | \psi_{n,\lambda} \rangle \\ &= 0, \end{aligned}$$

because  $\langle \psi_{n,\lambda} | \psi_{n,\lambda} \rangle$  has the constant value of 1 irrespective of  $\lambda$ . Combining this with our previous expression for  $\partial E_{n,\lambda} / \partial \lambda$ , we see that only the second term on the right-hand side of this equation survives and so we obtain

$$\frac{\partial E_{n,\lambda}}{\partial \lambda} = \left\langle \psi_{n,\lambda} \middle| \frac{\partial \hat{H}_\lambda}{\partial \lambda} \middle| \psi_{n,\lambda} \right\rangle,$$

as required.

**Comments** (1) Because the energy eigenfunctions depend on the parameter  $\lambda$ , the derivative of the expectation value in principle involves derivatives of the eigenfunctions. The key point about the Hellmann–Feynman theorem is that these derivatives cancel out, and we are left only with the expectation value of the derivative of the Hamiltonian operator with respect to  $\lambda$ .

(2) When using the Hellmann–Feynman theorem we generally omit the subscript  $\lambda$  in our notation for the Hamiltonian operator and the energy eigenvalues and eigenfunctions. It is included in the above proof to make the dependence on  $\lambda$  explicit, but we have no need to include it when applying the theorem – we just take the parameter  $\lambda$  to have its physically appropriate value.

**Exercise 4.6** (a) From the given Hamiltonian operator and energy eigenvalue, we have

$$\frac{\partial \hat{H}}{\partial C} = \frac{1}{2} x^2 \quad \text{and} \quad \frac{\partial E_n}{\partial C} = \frac{1}{2} \left( n + \frac{1}{2} \right) \hbar \left( \frac{1}{Cm} \right)^{1/2} = \frac{E_n}{2C},$$

so the Hellmann–Feynman theorem gives

$$\frac{E_n}{2C} = \langle \psi_n | \frac{1}{2} x^2 | \psi_n \rangle = \langle \frac{1}{2} x^2 \rangle.$$

Multiplying both sides by  $C$  then gives

$$\frac{1}{2} E_n = \langle \frac{1}{2} C x^2 \rangle = \langle E_{\text{pot}} \rangle,$$

as required.

(b) From the given Hamiltonian operator and energy eigenvalue, we have

$$\frac{\partial \hat{H}}{\partial e} = -\frac{2e}{4\pi\epsilon_0 r} \quad \text{and} \quad \frac{\partial E_n}{\partial e} = -\frac{4e^3}{(4\pi\epsilon_0)^2} \frac{\mu}{2\hbar^2} \frac{1}{n^2} = 4\frac{E_n}{e}$$

so the Hellmann–Feynman theorem gives

$$4\frac{E_n}{e} = \langle \psi_{nlm} | -\frac{2e}{4\pi\epsilon_0 r} | \psi_{nlm} \rangle.$$

Multiplying both sides by  $e/2$  then gives

$$2E_n = \langle \psi_{nlm} | -\frac{e^2}{4\pi\epsilon_0 r} | \psi_{nlm} \rangle = \langle E_{\text{pot}} \rangle$$

as required.

Note: Since  $E_n$  is negative, this implies that  $\langle E_{\text{pot}} \rangle$  is twice as negative as the energy eigenvalue. This is compensated by the fact that  $\langle E_{\text{kin}} \rangle$  has the positive value  $-E_n$ , so  $\langle E_{\text{kin}} \rangle + \langle E_{\text{pot}} \rangle = -E_n + 2E_n = E_n$ .

**Comments** (1) The Hellmann–Feynman theorem is not a formal part of the course, so you need not remember it. As you have seen here, the theorem is useful if differentiating the Hamiltonian operator with respect to a parameter gives another operator whose expectation value in an energy eigenstate is of interest. We need to have an explicit formula for the energy eigenvalues.

(2) Remembering that the total energy is  $E_{\text{kin}} + E_{\text{pot}}$ , the results derived in this question can be re-expressed as follows. In any energy eigenstate of a one-dimensional harmonic oscillator,  $\langle E_{\text{kin}} \rangle = \langle E_{\text{pot}} \rangle$ , and in any energy eigenstate of a hydrogen atom in the Coulomb model,  $\langle E_{\text{kin}} \rangle = -\frac{1}{2}\langle E_{\text{pot}} \rangle$ . The latter result is possible because the expectation value of the potential energy is negative in this case.

## Topic 5 — Variational method

**Solution 5.1** (a) We have

$$\frac{d}{dx} e^{-\alpha x^2/2} = -\alpha x e^{-\alpha x^2/2}$$

so

$$\frac{d^2}{dx^2} e^{-\alpha x^2/2} = (-\alpha + \alpha^2 x^2) e^{-\alpha x^2/2}.$$

Hence,

$$\begin{aligned} \frac{\langle \phi_t | -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} | \phi_t \rangle}{\langle \phi_t | \phi_t \rangle} &= \frac{\frac{\hbar^2}{2m} \left( \alpha \int_{-\infty}^{\infty} e^{-\alpha x^2} dx - \alpha^2 \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx \right)}{\int_{-\infty}^{\infty} e^{-\alpha x^2} dx} \\ &= \frac{\hbar^2}{2m} \alpha - \frac{\hbar^2}{2m} \alpha^2 \times \frac{\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx}{\int_{-\infty}^{\infty} e^{-\alpha x^2} dx} \\ &= \frac{\hbar^2}{2m} \alpha - \frac{\hbar^2}{2m} \alpha^2 \times \frac{1}{2\alpha} \\ &= \frac{\hbar^2}{4m} \alpha. \end{aligned}$$

Also,

$$\frac{\langle \phi_t | V | \phi_t \rangle}{\langle \phi_t | \phi_t \rangle} = -V_0 \frac{\int_0^L e^{-\alpha x^2} dx}{\int_{-\infty}^{\infty} e^{-\alpha x^2} dx}$$

Change the variable of integration to  $u = \sqrt{\alpha}x$ , then

$$\frac{\langle \phi_t | V | \phi_t \rangle}{\langle \phi_t | \phi_t \rangle} = -V_0 \frac{\int_0^{\sqrt{\alpha}L} e^{-u^2} du}{\int_{-\infty}^{\infty} e^{-u^2} du} = -\frac{V_0}{\sqrt{\pi}} \int_0^{\sqrt{\alpha}L} e^{-u^2} du.$$

So

$$E_t \equiv \frac{\langle \phi_t | \hat{H} | \phi_t \rangle}{\langle \phi_t | \phi_t \rangle} = \frac{\hbar^2}{4m} \alpha - \frac{V_0}{\sqrt{\pi}} \int_0^{\sqrt{\alpha}L} e^{-u^2} du,$$

as required.

(b) When  $\alpha$  is positive, but very small, we can approximate the integral by

$$\int_0^{\sqrt{\alpha}L} e^{-u^2} du \simeq e^0 \times \sqrt{\alpha}L = \sqrt{\alpha}L.$$

So, in the limit of small positive  $\alpha$ , we have

$$E_t = \frac{\hbar^2}{4m} \alpha - \frac{V_0}{\sqrt{\pi}} \sqrt{\alpha}L,$$

and this is negative when

$$\frac{\hbar^2}{4m} \sqrt{\alpha} < \frac{V_0 L}{\sqrt{\pi}},$$

i.e. when

$$0 < \alpha < \frac{16m^2 V_0^2 L^2}{\hbar^4 \pi},$$

which can always be achieved. The exact ground-state energy must be smaller than any variational estimate, so the exact ground-state energy is always negative (below the top of the well) no matter how small  $V_0$  and  $L$  may be.

**Comment** We have shown that any finite square well in one dimension (no matter how narrow or shallow) has at least one bound state. This result was quoted in Book 1, but not proved there. However, this result turns out to be specific to one-dimensional wells. It is possible to have finite wells in two or three dimensions that are so narrow and/or shallow that they have no bound states.

**Solution 5.2** Using the identity given in the question, we have

$$\begin{aligned} -\frac{\hbar^2}{2m} \nabla^2 \phi_t(r) &= -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} e^{-r/a} \right) \\ &= \frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left( \frac{r^2}{a} e^{-r/a} \right) \\ &= \frac{\hbar^2}{2m} \frac{1}{r^2} \left( \frac{2r}{a} - \frac{r^2}{a^2} \right) e^{-r/a} \\ &= \frac{\hbar^2}{2m} \left( \frac{2}{ar} - \frac{1}{a^2} \right) e^{-r/a}. \end{aligned}$$

Thus,

$$\hat{H} \phi_t(r) = \frac{\hbar^2}{2m} \left( \frac{2}{ar} - \frac{1}{a^2} \right) e^{-r/a} + \frac{1}{2} m \omega_0^2 r^2 e^{-r/a}.$$

We therefore have

$$\begin{aligned} \langle \phi_t | \hat{H} | \phi_t \rangle &= \int_0^{2\pi} \int_0^\pi \int_0^\infty e^{-r/a} \left[ \frac{\hbar^2}{2m} \left( \frac{2}{ar} - \frac{1}{a^2} \right) + \frac{1}{2} m \omega_0^2 r^2 \right] e^{-r/a} r^2 \sin \theta dr d\theta d\phi \\ &= 4\pi \int_0^\infty \left[ \frac{\hbar^2}{ma} r - \frac{\hbar^2}{2ma^2} r^2 + \frac{1}{2} m \omega_0^2 r^4 \right] e^{-2r/a} dr. \end{aligned}$$

Using the standard integral given in the question,

$$\begin{aligned}
 \langle \phi_t | \hat{H} | \phi_t \rangle &= 4\pi \left( \frac{\hbar^2}{ma} 1! \left( \frac{a}{2} \right)^2 - \frac{\hbar^2}{2ma^2} 2! \left( \frac{a}{2} \right)^3 + \frac{1}{2} m\omega_0^2 4! \left( \frac{a}{2} \right)^5 \right) \\
 &= 4\pi \left( \frac{\hbar^2 a}{4m} - \frac{\hbar^2 a}{8m} + \frac{3}{8} m\omega_0^2 a^5 \right) \\
 &= \pi \left( \frac{\hbar^2 a}{2m} + \frac{3}{2} m\omega_0^2 a^5 \right).
 \end{aligned}$$

We also have

$$\begin{aligned}
 \langle \phi_t | \phi_t \rangle &= \int_0^{2\pi} \int_0^\pi \int_0^\infty e^{-2r/a} r^2 \sin \theta \, dr \, d\theta \, d\phi \\
 &= 4\pi \int_0^\infty r^2 e^{-2r/a} \, dr \\
 &= 4\pi 2! \left( \frac{a}{2} \right)^3 \\
 &= \pi a^3,
 \end{aligned}$$

so

$$E_t = \frac{\langle \phi_t | \hat{H} | \phi_t \rangle}{\langle \phi_t | \phi_t \rangle} = \frac{\hbar^2}{2ma^2} + \frac{3}{2} m\omega_0^2 a^2.$$

The minimum value is obtained by setting

$$0 = \frac{dE_t}{da} = -\frac{\hbar^2}{ma^3} + 3m\omega_0^2 a,$$

so

$$a^2 = \frac{1}{\sqrt{3}} \frac{\hbar}{m\omega_0}$$

and the estimated ground-state energy eigenvalue is

$$E_{t,\min} = \frac{\hbar^2}{2m} \frac{\sqrt{3}m\omega_0}{\hbar} + \frac{3}{2} m\omega_0^2 \frac{\hbar}{\sqrt{3}m\omega_0} = \sqrt{3} \hbar \omega_0.$$

**Comment** This estimate is about 15% greater than the exact ground-state energy (see next exercise). The variational method always produces an estimate that is greater than, or equal to, the ground-state energy.

**Solution 5.3** We have

$$\begin{aligned}
 -\frac{\hbar^2}{2m} \nabla^2 \phi_t(r) &= -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} e^{-r^2/2a^2} \right) \\
 &= -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \left( \frac{-r}{a^2} e^{-r^2/2a^2} \right) \right) \\
 &= \frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left( \frac{r^3}{a^2} e^{-r^2/2a^2} \right) \\
 &= \frac{\hbar^2}{2m} \frac{1}{r^2} \left( \frac{3r^2}{a^2} - \frac{r^4}{a^4} \right) e^{-r^2/2a^2} \\
 &= \frac{\hbar^2}{2ma^2} \left( 3 - \frac{r^2}{a^2} \right) e^{-r^2/2a^2}.
 \end{aligned}$$

Thus,

$$\hat{H}\phi_t(r) = \frac{\hbar^2}{2ma^2} \left( 3 - \frac{r^2}{a^2} \right) e^{-r^2/2a^2} + \frac{1}{2} m\omega_0^2 r^2 e^{-r^2/2a^2}.$$



We therefore have

$$\begin{aligned}\langle \phi_t | \hat{H} | \phi_t \rangle &= \int_0^{2\pi} \int_0^\pi \int_0^\infty e^{-r^2/2a^2} \left[ \frac{\hbar^2}{2ma^2} \left( 3 - \frac{r^2}{a^2} \right) + \frac{1}{2} m\omega_0^2 r^2 \right] e^{-r^2/2a^2} r^2 \sin \theta \, dr \, d\theta \, d\phi \\ &= 4\pi \int_0^\infty \left[ \frac{3\hbar^2}{2ma^2} r^2 - \frac{\hbar^2}{2ma^4} r^4 + \frac{1}{2} m\omega_0^2 r^4 \right] e^{-r^2/a^2} \, dr.\end{aligned}$$

Using the standard integrals given in the question,

$$\begin{aligned}\langle \phi_t | \hat{H} | \phi_t \rangle &= 4\pi \left( \frac{3\hbar^2}{2ma^2} \frac{\sqrt{\pi}}{4} a^3 - \frac{\hbar^2}{2ma^4} \frac{3\sqrt{\pi}}{8} a^5 + \frac{1}{2} m\omega_0^2 \frac{3\sqrt{\pi}}{8} a^5 \right) \\ &= 12\pi\sqrt{\pi} \left( \frac{\hbar^2}{8m} a - \frac{\hbar^2}{16m} a + \frac{1}{16} m\omega_0^2 a^5 \right) \\ &= \frac{3\pi\sqrt{\pi}}{4} \left( \frac{\hbar^2}{m} a + m\omega_0^2 a^5 \right).\end{aligned}$$

We also have

$$\begin{aligned}\langle \phi_t | \phi_t \rangle &= \int_0^{2\pi} \int_0^\pi \int_0^\infty e^{-r^2/a^2} r^2 \sin \theta \, dr \, d\theta \, d\phi \\ &= 4\pi \int_0^\infty r^2 e^{-r^2/a^2} \, dr \\ &= 4\pi \frac{\sqrt{\pi}}{4} a^3 \\ &= \pi\sqrt{\pi} a^3,\end{aligned}$$

so

$$E_t = \frac{\langle \phi_t | \hat{H} | \phi_t \rangle}{\langle \phi_t | \phi_t \rangle} = \frac{3}{4} \left( \frac{\hbar^2}{ma^2} + m\omega_0^2 a^2 \right).$$

The minimum value is obtained by setting

$$0 = \frac{dE_t}{da} = \frac{3}{4} \left( -\frac{2\hbar^2}{ma^3} + 2m\omega_0^2 a \right),$$

so

$$a^2 = \frac{\hbar}{m\omega_0}$$

and the estimated ground-state energy eigenvalue is

$$E_{t,\min} = \frac{3}{4} \left( \frac{\hbar^2}{m} \frac{m\omega_0}{\hbar} + m\omega_0^2 \frac{\hbar}{m\omega_0} \right) = \frac{3}{2} \hbar\omega_0.$$

**Comment** This estimate turns out to be exact because the trial function  $e^{-r^2/a^2}$  happens to include the exact ground-state energy eigenfunction (which has  $a^2 = \hbar/m\omega_0$ ). The estimate made in Exercise 5.2 is slightly greater than this, because a trial function of the form  $e^{-r/a}$  is less accurate for this system.

## Topic 6 — Hydrogen-like systems

**Solution 6.1** For helium-4, we have  $m = 7360m_e$ , so the reduced mass is

$$\mu = \frac{207 \times 7360}{207 + 7360} m_e = 201.3m_e.$$

We are told that the reduced mass of hydrogen can be taken to be  $m_e$ , so  $\mu/\mu_H = 201.3$ . For helium,  $Z = 2$ , so the scaled Rydberg energy is

$$E_R^{\text{scaled}} = Z^2 \frac{\mu}{\mu_H} E_R = 2^2 \times 201.3 \times 13.6 \text{ eV} = 1.10 \times 10^4 \text{ eV}$$

and the scaled Bohr radius is

$$a_0^{\text{scaled}} = \frac{1}{Z} \frac{\mu_H}{\mu} a_0 = 5.29 \times 10^{-11} \text{ m} / (201.3 \times 2) = 1.31 \times 10^{-13} \text{ m}.$$

**Comment** This calculation assumes that the muon is mainly outside the helium-4 nucleus, which is justified because the nuclear radius of helium-4 is of order  $1.7 \times 10^{-15} \text{ m}$ .

**Solution 6.2** The reduced mass of positronium is

$$\mu = \frac{m_e^2}{m_e + m_e} = \frac{m_e}{2}.$$

We are told that the reduced mass of hydrogen can be taken to be  $m_e$ , so  $\mu/\mu_H = 1/2$ . The scaled Bohr radius is

$$\frac{\mu_H}{\mu} a_0 = 2a_0 = 2 \times 5.29 \times 10^{-11} \text{ m} = 1.06 \times 10^{-10} \text{ m},$$

and the scaled Rydberg energy is

$$E_R^{\text{scaled}} = \frac{\mu}{\mu_H} E_R = \frac{1}{2} \times 13.6 \text{ eV} = 6.8 \text{ eV},$$

so the ground-state energy is

$$E_1 = -\frac{E_R^{\text{scaled}}}{1^2} = -E_R^{\text{scaled}} = -6.8 \text{ eV}.$$

**Comment** The usual formula for the scaled Rydberg energy in an atom involves the atomic number  $Z$ , which appears because the charge of the nucleus is  $Ze$ , where  $e$  is the magnitude of the charge of an electron. In positronium, the positron plays the role of the nucleus in an atom, so in this case  $Z = 1$ .

## Topic 7 — Relativistic hydrogen atom

**Solution 7.1** The additional effects include:

- A relativistic correction to the kinetic energy
- the spin-orbit interaction (for  $l \neq 0$ )
- the Darwin term (for  $l = 0$ )
- the Lamb shift
- the finite size of the proton
- the magnetic interaction between the magnetic dipoles of the electron and the proton.

**Comment** The first three effects give rise to fine structure (corrections of order  $\alpha^2$ , where  $\alpha \simeq 1/137$  is the fine structure constant) while the last three effects give rise to hyperfine structure.

**Solution 7.2** (a) In the absence of a spin–orbit interaction the states are:

$$\begin{aligned} |n, l, m, m_s\rangle &= |2, 0, 0, +\tfrac{1}{2}\rangle & |n, l, m, m_s\rangle &= |2, 0, 0, -\tfrac{1}{2}\rangle \\ |n, l, m, m_s\rangle &= |2, 1, 1, +\tfrac{1}{2}\rangle & |n, l, m, m_s\rangle &= |2, 1, 1, -\tfrac{1}{2}\rangle \\ |n, l, m, m_s\rangle &= |2, 1, 0, +\tfrac{1}{2}\rangle & |n, l, m, m_s\rangle &= |2, 1, 0, -\tfrac{1}{2}\rangle \\ |n, l, m, m_s\rangle &= |2, 1, -1, +\tfrac{1}{2}\rangle & |n, l, m, m_s\rangle &= |2, 1, -1, -\tfrac{1}{2}\rangle. \end{aligned}$$

(b) In the presence of a spin–orbit interaction, we use the rules that  $j = l \pm \frac{1}{2}$  for  $l \neq 0$  and  $j = \frac{1}{2}$  for  $l = 0$ , together with the fact that there are  $2j + 1$  values of  $m_j$ , ranging in integer steps from  $-j$  to  $+j$ .

For  $n = 2$ , the allowed values of  $l$  and  $s$  are

$$l = 0 \text{ or } 1 \quad \text{and} \quad s = \frac{1}{2}$$

For  $l = 0$ , the only allowed value of  $j$  is  $\frac{1}{2}$ , so the two possible states are:

$$|n, l, j, m_j\rangle = |2, 0, \tfrac{1}{2}, -\tfrac{1}{2}\rangle, \quad |n, l, j, m_j\rangle = |2, 0, \tfrac{1}{2}, +\tfrac{1}{2}\rangle.$$

For  $l = 1$ , the allowed values of  $j$  are  $\frac{1}{2}$  and  $\frac{3}{2}$ , so the possible states are:

$$\begin{aligned} |n, l, j, m_j\rangle &= |2, 1, \tfrac{1}{2}, -\tfrac{1}{2}\rangle, & |n, l, j, m_j\rangle &= |2, 1, \tfrac{1}{2}, +\tfrac{1}{2}\rangle, \\ |n, l, j, m_j\rangle &= |2, 1, \tfrac{3}{2}, -\tfrac{3}{2}\rangle, & |n, l, j, m_j\rangle &= |2, 1, \tfrac{3}{2}, -\tfrac{1}{2}\rangle, \\ |n, l, j, m_j\rangle &= |2, 1, \tfrac{3}{2}, +\tfrac{1}{2}\rangle, & |n, l, j, m_j\rangle &= |2, 1, \tfrac{3}{2}, +\tfrac{3}{2}\rangle. \end{aligned}$$

According to relativistic quantum mechanics, energy levels depend on  $n$  and  $j$ , but not on  $l$  or  $m_j$ , so each  $n = 2$  energy level splits into two, with four degenerate states

$$|n, l, j, m_j\rangle = |2, 0, \tfrac{1}{2}, -\tfrac{1}{2}\rangle, \quad |2, 0, \tfrac{1}{2}, +\tfrac{1}{2}\rangle, \quad |2, 1, \tfrac{1}{2}, -\tfrac{1}{2}\rangle, \quad |2, 1, \tfrac{1}{2}, +\tfrac{1}{2}\rangle,$$

and four degenerate states

$$|n, l, j, m_j\rangle = |2, 1, \tfrac{3}{2}, -\tfrac{3}{2}\rangle, \quad |2, 1, \tfrac{3}{2}, -\tfrac{1}{2}\rangle, \quad |2, 1, \tfrac{3}{2}, +\tfrac{1}{2}\rangle, \quad |2, 1, \tfrac{3}{2}, +\tfrac{3}{2}\rangle.$$

**Comment** In the Coulomb model of a hydrogen atom, the energy level with  $n = 2$  comprises 8 different states characterized by the quantum numbers  $n, l, m$  and  $m_s$ . When the spin–orbit interaction is taken into account, these states combine together to form new states labelled by the quantum numbers  $n, l, j$  and  $m_j$ . It is a good check to note that we still have 8 different quantum states (though these are now split into two energy levels).

**Solution 7.3** The spin–orbit interaction is proportional to  $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ . It is non-zero for all states with  $l \neq 0$ , and vanishes for states with  $l = 0$ .

The Darwin term involves  $\nabla^2 V(\mathbf{r})$ , where  $V(\mathbf{r})$  is the Coulomb potential energy function due to the proton. It is a result of electrostatics that  $\nabla^2 V(\mathbf{r}) = 0$  in regions where there is no charge (in this case, outside the proton). Taking the proton to be point-like, the first-order correction due to the Darwin term is only non-zero for energy eigenfunctions that do not vanish at  $r = 0$ . Because of the centrifugal barrier in a hydrogen atom, only the  $l = 0$  states meet this criterion.

**Comment** Each hydrogen atom energy eigenfunction involves a radial function that behaves as  $r^l$  as  $r \rightarrow 0$ , so only the  $l = 0$  eigenfunction is non-zero at  $r = 0$ .

**Solution 7.4** (a) We have

$$\hat{\mathbf{J}}^2 = (\hat{\mathbf{L}} + \hat{\mathbf{S}}) \cdot (\hat{\mathbf{L}} + \hat{\mathbf{S}}) = \hat{\mathbf{L}}^2 + 2\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} + \hat{\mathbf{S}}^2,$$

so

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{1}{2} (\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2).$$

(b) The perturbation due to the spin–orbit correction is of the form

$$\delta\hat{H}_{\text{so}} = V_{\text{so}}(r) \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}.$$

In first-order perturbation theory, the ratio of the spin-orbit corrections in states  $|A\rangle$  and  $|B\rangle$  is

$$\frac{E_A^{(1)}}{E_B^{(1)}} = \frac{\langle A | \delta \hat{H}_{so} | A \rangle}{\langle B | \delta \hat{H}_{so} | B \rangle}$$

In evaluating a matrix element such as  $\langle A | \delta \hat{H}_{so} | A \rangle$ , we must integrate over  $r$ ,  $\theta$  and  $\phi$ , and also take the inner product with respect to electron spin. The integral over  $r$  is the same for both  $|A\rangle$  and  $|B\rangle$  because both these states have the same  $n$  and  $l$  quantum numbers, and therefore have the same dependence on  $r$ . We therefore have

$$\frac{E_A^{(1)}}{E_B^{(1)}} = \frac{\langle A | \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} | A \rangle}{\langle B | \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} | B \rangle}$$

The state  $|A\rangle$ , with  $j = l + \frac{1}{2}$ , gives

$$\begin{aligned} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} | A \rangle &= \frac{1}{2} (\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2) | A \rangle \\ &= \frac{1}{2} \left( (l + \frac{1}{2})(l + \frac{3}{2}) - l(l + 1) - \frac{1}{2}(\frac{1}{2} + 1) \right) | A \rangle \\ &= \frac{1}{2} \left( l^2 + 2l + \frac{3}{4} - l^2 - l - \frac{3}{4} \right) | A \rangle \\ &= \frac{l}{2} | A \rangle, \end{aligned}$$

so

$$\langle A | \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} | A \rangle = \frac{l}{2}.$$

The state  $|B\rangle$ , with  $j = l - \frac{1}{2}$ , gives

$$\begin{aligned} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} | B \rangle &= \frac{1}{2} (\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2) | B \rangle \\ &= \frac{1}{2} \left( (l - \frac{1}{2})(l + \frac{1}{2}) - l(l + 1) - \frac{1}{2}(\frac{1}{2} + 1) \right) | B \rangle \\ &= \frac{1}{2} \left( l^2 - \frac{1}{4} - l^2 - l - \frac{3}{4} \right) | B \rangle \\ &= -\frac{(l + 1)}{2} | B \rangle. \end{aligned}$$

so

$$\langle B | \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} | B \rangle = -\frac{(l + 1)}{2}.$$

Consequently,

$$\frac{E_A^{(1)}}{E_B^{(1)}} = -\frac{l}{l + 1}.$$

**Comments** (1) On multiplying out the brackets in  $(\hat{\mathbf{L}} + \hat{\mathbf{S}}) \cdot (\hat{\mathbf{L}} + \hat{\mathbf{S}})$ , we have used the fact that  $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \hat{\mathbf{S}} \cdot \hat{\mathbf{L}}$ . This is because the orbital angular momentum operators  $\hat{L}_x$ ,  $\hat{L}_y$  and  $\hat{L}_z$  (which act on the spatial functions) commute with the spin angular momentum  $\hat{S}_x$ ,  $\hat{S}_y$  and  $\hat{S}_z$  (which act on spin kets).

(2) In the presence of the spin-orbit interaction, the energy eigenstates of a hydrogen atom are labelled by the quantum numbers  $n$ ,  $l$ ,  $j$  and  $m_j$ . Moreover, the spin quantum number of all states is  $s = \frac{1}{2}$ . So each energy eigenstate is an eigenfunction of  $\hat{\mathbf{J}}^2$ ,  $\hat{\mathbf{L}}^2$  and  $\hat{\mathbf{S}}^2$ , and that is why it is useful to express  $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$  in terms of these operators.

(3) The spin-orbit interaction increases the energy of the state with  $j = l + \frac{1}{2}$  and decreases the energy of the state with  $j = l - \frac{1}{2}$ .

## Topic 8 — Many-electron atoms

**Solution 8.1** In the central-field approximation, each electron is in a spherically-symmetric potential energy well. This allows the time-independent Schrödinger equation to be separated; the energy eigenfunctions can be written as products of a radial function  $R(r)$  and an angular function,  $Y(\theta, \phi)$ . The angular function satisfies the same angular differential equation as for a hydrogen atom, and has spherical harmonic solutions  $Y_{lm}(\theta, \phi)$ , labelled by orbital angular momentum and magnetic quantum numbers  $l$  and  $m$ . The radial equation is not the same as for a hydrogen atom, but its solutions can still be labelled by an index  $n$  (as well as by  $l$ ).

**Comment** Another way of understanding this is to note that, with a spherically-symmetric potential energy function, the Hamiltonian operator commutes with  $\hat{L}^2$  and  $\hat{L}_z$  and this allows the energy eigenfunctions to be chosen so that they are also eigenfunctions of  $\hat{L}^2$  and  $\hat{L}_z$ , labelled by the corresponding quantum numbers  $l$  and  $m$ .

**Solution 8.2** (a) For  $n = 1$ , the only atomic shell is 1s ( $l = 0$ , capacity 2 electrons).

For  $n = 2$ , the atomic shells are 2s ( $l = 0$ , capacity 2 electrons) and 2p ( $l = 1$ , capacity 6 electrons).

For  $n = 3$ , the atomic shells are 3s ( $l = 0$ , capacity 2 electrons), 3p ( $l = 1$ , capacity 6 electrons) and 3d ( $l = 2$ , capacity 10 electrons).

For  $n = 4$ , the atomic shells are 4s ( $l = 0$ , capacity 2 electrons), 4p ( $l = 1$ , capacity 6 electrons) and 4d ( $l = 2$ , capacity 10 electrons) and 4f ( $l = 3$ , capacity 14 electrons).

(b) The energy ordering of these shells is: 1s, 2s, 2p, 3s, 3p, 4s, 3d, ...

Silicon has 14 electrons so the ground-state electronic configuration is

$$1s^2 2s^2 2p^6 3s^2 3p^2.$$

Iron has 26 electrons so the ground-state electronic configuration is

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6.$$

**Comment** The concept of an electronic configuration, specified by the numbers of electrons with given  $n$  and  $l$  quantum numbers, is based on the central-field approximation. Beyond this approximation, residual electron–electron interactions split the ground-state configuration into various atomic terms and the spin–orbit interaction further splits the atomic terms into atomic levels.

## Topic 9 — Atomic terms and levels

**Solution 9.1** The possible values of  $L$  range in integer steps from  $|l_1 - l_2|$  to  $l_1 + l_2$ , so the possible values are  $L = 2$ ,  $L = 3$  and  $L = 4$ .

The possible values of  $S$  range in integer steps from  $|s_1 - s_2|$  to  $s_1 + s_2$ , so the possible values are  $S = 0$  and  $S = 1$ .

The corresponding atomic terms are:

$$(L = 2, S = 0), \quad (L = 2, S = 1),$$

$$(L = 3, S = 0), \quad (L = 3, S = 1),$$

$$(L = 4, S = 0), \quad (L = 4, S = 1).$$

These are labelled, respectively, by the spectroscopic symbols  $^1D$ ,  $^3D$ ,  $^1F$ ,  $^3F$ ,  $^1G$  and  $^3G$ .

**Comments** (1) Residual electron–electron interactions produce atomic terms with definite values of  $L$  and  $S$  for the whole atom. (We are implicitly assuming that the  $LS$ -coupling approximation is valid, so this scheme is not undermined by the spin–orbit couplings of the orbital and angular momenta of individual electrons.)

(2) The total number of states associated with the given configuration can be calculated from the  $(l, s)$  quantum numbers of the two valence electrons. This gives  $(3 \times 2) \times (7 \times 2) = 84$  states. We can also calculate the number of states associated with each of the atomic terms.  $^1D$  has 5 states,  $^3D$  has  $5 \times 3 = 15$  states,  $^1F$  has 7 states,  $^3F$  has  $7 \times 3 = 21$  states,  $^1G$  has 9 states and  $^3G$  has  $9 \times 3 = 27$  states. It is a good check to note that  $5 + 15 + 7 + 21 + 9 + 27 = 84$ .

**Solution 9.2** The two electrons in a helium atom are identical fermions, so must be described by an antisymmetric total wave function. The singlet spin state is antisymmetric, so must be accompanied by a symmetric spatial wave function. The triplet spin states are symmetric, so must be accompanied by an antisymmetric spatial wave function.

In a state described by a symmetric spatial wave function, the two electrons huddle together and experience a strong positive potential energy from electron–electron repulsion. In a state described by an antisymmetric spatial wave function, the two electrons are segregated and experience a weaker positive potential energy from electron–electron repulsion.

Consequently, the singlet state, which is accompanied by a symmetric spatial wave function, has a higher energy than the triplet states, which are accompanied by an antisymmetric spatial wave function.

**Comments** (1) The energy splitting between singlet and triplet states can be found using first-order perturbation theory, where the perturbation is the repulsive potential energy between the two electrons.

(2) This is an example of the energy splitting between different atomic terms that can result from residual electron–electron interactions (i.e. electron–electron interactions ignored in the central-field approximation).

## Topic 10 — Molecules

**Solution 10.1** A diatomic  $\text{Be}_2$  molecule has 8 electrons. Each  $\sigma$  molecular orbital holds up to 2 electrons, so the ground-state configuration of a  $\text{Be}_2$  molecule is

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2.$$

There are four electrons in bonding orbitals and four electrons in antibonding orbitals, so the formal bond order is  $(4 - 4)/2 = 0$ .

We would not expect the  $\text{Be}_2$  molecule to be strongly bound. Because we are only working within the LCAO approximation, we can expect either a very weakly bound molecule, with a small dissociation energy, or an unstable molecule, but cannot be more precise than this.

**Comment** As shown in Table 6.2 of Book 3, the spectroscopic binding energy of  $\text{Be}_2$  is only 0.10 eV, which is an order-of-magnitude smaller than the spectroscopic binding energies of homonuclear diatomic molecules formed from atoms near Be in its row of the Periodic Table.

**Solution 10.2** (a) The Born–Oppenheimer approximation is based on the classical notion that nuclei are much more massive than electrons and so are more sluggish. So far as the electrons are concerned, the Born–Oppenheimer approximation treats the nuclei as being in fixed positions. For a given set of nuclear positions, the time-independent Schrödinger equation for the electrons is solved (approximately if necessary) to find the electronic energy eigenfunctions and eigenvalues. For each electronic energy eigenvalue, the eigenvalue is added to the mutual potential energy function of the nuclei to give the total static energy of the molecule. The total static energy is a function of the nuclear positions, and this function provides an effective potential energy function which appears in the time-independent Schrödinger equation associated with the motions of the nuclei. There are different nuclear time-independent Schrödinger equations for each electronic energy eigenvalue.

(b) For a given electronic energy eigenvalue in a diatomic molecule, an energy curve is a plot of the total static energy as a function of the internuclear distance. Assumption of the Born–Oppenheimer approximation allows us to calculate the electronic energy eigenvalue, and hence the total static energy, of a molecule at a series of fixed internuclear distances.

**Comment** The Born–Oppenheimer approximation is *not* the same as the method of separation of variables. The time-independent Schrödinger equation for a molecule cannot be separated into independent equations for the electrons and nuclei, but the Born–Oppenheimer approximation does the next best thing. The nuclear coordinates appear in both the electronic and nuclear time-independent Schrödinger equations, but are given fixed values in the electronic time-independent Schrödinger equation. The electronic coordinates appear only in the electronic time-independent Schrödinger equation; in the nuclear time-independent Schrödinger equation the electronic degrees of freedom are replaced by an electronic energy eigenvalue (which depends on the nuclear positions). The coupling between the electronic and nuclear motions is revealed by the existence of different nuclear time-independent Schrödinger equations for different electronic energy eigenvalues.

**Solution 10.3** (a) The total static energy is the sum of the electronic energy eigenvalue and the proton–proton repulsion energy, and so is given by

$$\begin{aligned} E_{\text{stat}}(R) &= E_{\text{el}}(R) + \frac{e^2}{4\pi\epsilon_0 R} \\ &= \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{5} \frac{a^4}{R^5} - \frac{2}{R} + \frac{1}{R} \right) \\ &= \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{5} \frac{a^4}{R^5} - \frac{1}{R} \right). \end{aligned}$$

(b) The total static energy, as a function of  $R$ , provides an effective potential energy function in which the protons move. The equilibrium proton–proton separation is the value of  $R$  for which this effective potential energy function is a minimum, and is given by the equation

$$\frac{dE_{\text{stat}}(R)}{dR} = \frac{e^2}{4\pi\epsilon_0} \left( -\frac{a^4}{R^6} + \frac{1}{R^2} \right) = 0,$$

which has the solution  $R = a$ . The spectroscopic dissociation energy  $D_{\text{eq}}$  is equal to the total static energy at infinite separation minus the total static energy at the equilibrium proton–proton separation, and is given by

$$\begin{aligned} D_{\text{eq}} &= 0 - E_{\text{stat}}(a) \\ &= -\frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{5} \frac{a^4}{a^5} - \frac{1}{a} \right) \\ &= \frac{e^2}{5\pi\epsilon_0 a}. \end{aligned}$$

**Comment** The directly-observed dissociation energy is slightly smaller than the spectroscopic dissociation energy because the protons have zero-point vibrational energy within the effective potential energy well, provided by  $E_{\text{stat}}(R)$ , making the minimum energy slightly greater (i.e. less negative) than  $E_{\text{stat}}(a)$ .

**Solution 10.4** (a) To ensure that  $\psi_1$  is normalized, we must have

$$\begin{aligned} 1 &= \langle \psi_1 | \psi_1 \rangle \\ &= |C|^2 (\langle \phi_{1s}^A | + \langle \phi_{1s}^B |) (| \phi_{1s}^A \rangle + | \phi_{1s}^B \rangle) \\ &= |C|^2 (\langle \phi_{1s}^A | \phi_{1s}^A \rangle + \langle \phi_{1s}^A | \phi_{1s}^B \rangle + \langle \phi_{1s}^B | \phi_{1s}^A \rangle + \langle \phi_{1s}^B | \phi_{1s}^B \rangle). \end{aligned}$$

Because the 1s orbitals centred on the two protons are normalized, we have

$$\langle \phi_{1s}^A | \phi_{1s}^A \rangle = \langle \phi_{1s}^B | \phi_{1s}^B \rangle = 1.$$

Because the 1s orbitals are described by real-valued functions, we have

$$\langle \phi_{1s}^A | \phi_{1s}^B \rangle = \langle \phi_{1s}^B | \phi_{1s}^A \rangle.$$

Hence

$$1 = 2|C|^2 (1 + \langle \phi_{1s}^A | \phi_{1s}^B \rangle)$$

so a suitable value of  $C$  is

$$C = \frac{1}{\sqrt{2(1 + \langle \phi_{1s}^A | \phi_{1s}^B \rangle)}}.$$

(b) The function  $\psi_1(\mathbf{r})$  leads to a high probability density of finding the electron in the region between the protons. This partially screens one proton from the other and promotes bonding. This mechanism does not apply for the function  $\psi_2(\mathbf{r})$ , which has a node midway between the protons.

**Comment** Note that atomic orbitals centred on different protons are not orthogonal, so it would be wrong to take  $C = 1/\sqrt{2}$ .

## Topic 11 — Solids

**Solution 11.1** Bloch's theorem states that, in an infinite crystal, the energy eigenfunctions of electrons can be written in the form

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}),$$

where  $\mathbf{k}$  is a real, constant vector and  $u_{\mathbf{k}}(\mathbf{r})$  is a periodic function, which may depend on  $\mathbf{k}$  and has the periodicity of the lattice:

$$u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{\mathbf{k}}(\mathbf{r}) \quad \text{for any lattice vector } \mathbf{R}.$$

Lattice points are separated by a lattice vector  $\mathbf{R}$ , and Bloch's theorem gives

$$|\psi(\mathbf{r} + \mathbf{R})|^2 = |u(\mathbf{r} + \mathbf{R})|^2 = |u(\mathbf{r})|^2 = |\psi(\mathbf{r})|^2.$$

**Comment** Each Bloch energy eigenfunction is the product of a periodic function (which is the same at each lattice point) and a plane wave function (which varies from one lattice point to another, unless  $\mathbf{k} = \mathbf{0}$ ). A typical electronic energy eigenfunction  $\psi$  does not have the periodicity of the lattice, but the probability density  $|\psi|^2$  does have this periodicity because the plane wave factor has unit modulus.

**Solution 11.2** (a) For any lattice vector  $\mathbf{R}_j$ , replacing  $\mathbf{r}$  by  $\mathbf{r} + \mathbf{R}_j$  throughout  $u(\mathbf{r})$  gives

$$\begin{aligned} u(\mathbf{r} + \mathbf{R}_j) &= \sum_i \phi(\mathbf{r} + \mathbf{R}_j - \mathbf{R}_i) e^{i\mathbf{k}\cdot(\mathbf{R}_i - \mathbf{r} - \mathbf{R}_j)} \\ &= \sum_i \phi(\mathbf{r} - (\mathbf{R}_i - \mathbf{R}_j)) e^{i\mathbf{k}\cdot(\mathbf{R}_i - \mathbf{R}_j - \mathbf{r})}. \end{aligned}$$

Here,  $\mathbf{R}_i - \mathbf{R}_j$  is another lattice vector,  $\mathbf{R}_l$ . Because the sum is over all lattice vectors in an infinite crystal, we obtain

$$u(\mathbf{r} + \mathbf{R}_j) = \sum_l \phi(\mathbf{r} - \mathbf{R}_l) e^{i\mathbf{k}\cdot(\mathbf{R}_l - \mathbf{r})} = u(\mathbf{r}).$$

Since  $u(\mathbf{r}) = u(\mathbf{r} + \mathbf{R}_j)$  for any lattice vector  $\mathbf{R}_j$ , we can say that  $u(\mathbf{r})$  has the periodicity of the lattice.

(b) Multiplying both sides of the expression for  $u(\mathbf{r})$  by  $e^{i\mathbf{k}\cdot\mathbf{r}}$  gives

$$\begin{aligned} u(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} &= e^{i\mathbf{k}\cdot\mathbf{r}} \sum_i \phi(\mathbf{r} - \mathbf{R}_i) e^{i\mathbf{k}\cdot(\mathbf{R}_i - \mathbf{r})} \\ &= \sum_i \phi(\mathbf{r} - \mathbf{R}_i) e^{i\mathbf{k}\cdot\mathbf{R}_i} \\ &= \psi(\mathbf{r}), \end{aligned}$$

so we conclude that  $\psi(\mathbf{r})$  is the product of a plane wave  $e^{i\mathbf{k}\cdot\mathbf{r}}$  and a function  $u(\mathbf{r})$  with the periodicity of the lattice, and therefore satisfies Bloch's theorem.

**Comment** The function  $u(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}$  is used in the tight-binding approximation for the electronic energy levels in a crystalline solid. It is used as the trial function in the variational method, even though there are no adjustable parameters in this case.

**Solution 11.3** For a hydrogen atom, the Rydberg energy is given by

$$E_R = \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{\mu}{2\hbar^2} = 13.6 \text{ eV}.$$

The corresponding result for a donor atom in germanium is obtained by replacing  $\epsilon_0$  by  $15.8\epsilon_0$ , and  $\mu$  by the effective electron mass  $m_e^* = 0.12 m_e$ , so the energy that must be supplied is

$$\frac{0.12}{15.8^2} \times 13.6 \text{ eV} = 6.5 \times 10^{-3} \text{ eV}.$$

**Comment** The typical thermal energy at room temperature is 0.025 eV, which is much larger than the ionization energy we have calculated. So, at room temperature, practically all pairs of donor atoms and electrons are ionized. At much lower temperatures the donor atoms and electrons form bound states, leading to a drop in the number of electrons in the conduction band and a drop in the electrical conductivity.



**Solution 11.4** A metal has a partly-filled energy band and a fixed number of current carriers. Its electrical conductivity is limited by deviations from a perfectly periodic crystal lattice. At normal temperatures a significant contribution from these deviations arises from vibrations of the crystal lattice, which increase with increasing temperature. The electrical conductivity of a metal therefore decreases with increasing temperature.

In a pure semiconductor at absolute zero, the valence band is full and the conduction band is empty, but the gap between the valence and conduction bands is small enough that, at higher temperatures, a significant number of electrons can be excited into the conduction band, leaving holes in the valence band. Conduction then takes place due to both electrons in the conduction band and holes in the valence band. The number of these electrons and holes increases with increasing temperature. This generally outweighs any effect due to an increase in lattice vibrations, so the electrical conductivity of a typical pure semiconductor increases with increasing temperature.

**Comment** In a doped semiconductor, there may be a range of temperatures over which almost all the impurities have donated electrons to the conduction band or produced holes in the valence band, but for which hardly any electrons have been excited from the valence band to the conduction band of the host semiconductor. In such a case, the electrical conductivity of the semiconductor may decrease with increasing temperature, as for a metal.

## Topic 12 — Interaction of light and matter

**Solution 12.1** (a) Absorption and stimulated emission have transition probabilities that can be predicted directly from first-order time-dependent perturbation theory.

(b) Quantum field theory is required for a fundamental understanding of spontaneous emission. In quantum field theory, the vacuum is not quiescent, but is a seething soup of virtual particles which can disturb an atom and shake it out of an excited stationary state.

**Comment** First-order time-dependent perturbation theory allows us to calculate a transition probability due to the presence of an external time-dependent perturbation. In absorption and stimulated emission the time-dependent perturbation is due to an externally-applied electromagnetic wave.

**Solution 12.2** According to the results of time-dependent perturbation theory, the transition probability from an initial state  $\psi_i$  to a final state  $\psi_f$  is proportional to

$$|\langle \psi_f | V(t) | \psi_i \rangle|^2 \propto |\langle \psi_f | r \cos \theta | \psi_i \rangle|^2$$

for light polarized along the  $z$ -direction.

For a hydrogen atom, the initial and final states are of the form

$$\begin{aligned}\psi_i(r, \theta, \phi) &= R_{n_i l_i}(r) \Theta_{l_i m_i}(\theta) e^{i m_i \phi} \\ \psi_f(r, \theta, \phi) &= R_{n_f l_f}(r) \Theta_{l_f m_f}(\theta) e^{i m_f \phi}.\end{aligned}$$

The transition probability therefore depends on the matrix element

$$\begin{aligned}\langle \psi_f | r \cos \theta | \psi_i \rangle &= \int_0^{2\pi} \int_0^\pi \int_0^\infty \psi_f^*(r, \theta, \phi) r \cos \theta \psi_i(r, \theta, \phi) r^2 \sin \theta \, dr \, d\theta \, d\phi \\ &= \int_0^{2\pi} e^{i(m_i - m_f)\phi} \, d\phi \int_0^\pi \Theta_{l_f m_f}^*(\theta) \Theta_{l_i m_i}(\theta) \cos \theta \sin \theta \, d\theta \int_0^\infty R_{n_f l_f}^*(r) R_{n_i l_i}(r) r^3 \, dr.\end{aligned}$$

For  $m_i \neq m_f$ , the integral over  $\phi$  gives

$$\int_0^{2\pi} e^{i(m_i - m_f)\phi} \, d\phi = \left[ \frac{e^{i(m_i - m_f)\phi}}{i(m_i - m_f)} \right]_{\phi=0}^{\phi=2\pi} = 0,$$

so the radiative transition will not take place (in first-order time-dependent perturbation theory) unless  $m_f = m_i$ .

**Comment** For radiative transitions induced by electromagnetic radiation polarized in the  $z$ -direction, there is a selection rule forbidding transitions with  $m_f \neq m_i$ . Note that this selection rule applies only to radiative transitions (it does not apply to transitions induced by atomic collisions) and it is restricted to transitions induced by electromagnetic radiation polarized in the  $z$ -direction. Moreover, it is only valid in first-order perturbation theory. Transitions with  $m_f \neq m_i$  may still occur in this case, but they are strongly inhibited and may not be noticeable compared to transitions with  $m_f = m_i$ . If they occur at all, they will produce very faint spectral lines.

**Solution 12.3** The solution follows the same lines as Exercise 12.2, but with

$$V(t) = f(t) r \sin \theta \cos \phi.$$

In this case, the relevant matrix element is

$$\begin{aligned} \langle \psi_f | r \sin \theta \cos \phi | \psi_i \rangle &= \int_0^{2\pi} \int_0^\pi \int_0^\infty \psi_f^*(r, \theta, \phi) r \sin \theta \cos \phi \psi_i(r, \theta, \phi) r^2 \sin \theta dr d\theta d\phi \\ &= \int_0^{2\pi} e^{i(m_i - m_f)\phi} \cos \phi d\phi \int_0^\pi \Theta_{l_f m_f}^*(\theta) \Theta_{l_i m_i}(\theta) \sin^2 \theta d\theta \int_0^\infty R_{n_f l_f}^*(r) R_{n_i l_i}(r) r^3 dr. \end{aligned}$$

For  $m_i = m_f$ , the integral over  $\phi$  gives

$$\int_0^{2\pi} \cos \phi d\phi = \left[ \sin \phi \right]_{\phi=0}^{\phi=2\pi} = 0,$$

so the radiative transition will not take place in this case (in first-order time-dependent perturbation theory).

**Comment** For electromagnetic radiation polarized in the  $x$ -direction, the selection rule forbids transitions with  $m_i = m_f$  (cf. Exercise 12.2). Again, this selection rule applies only for radiative transitions and for a particular polarization. It is valid within first-order perturbation theory, and so may not completely forbid very rare transitions.

**Solution 12.4** (a) The three types of radiative transition are as follows:

- (i) In *absorption*, a system absorbs a photon and makes a transition from a quantum state of lower energy to a quantum state of higher energy.
  - (ii) In *stimulated emission*, a system is stimulated by an incident photon to make a transition from a quantum state of higher energy to a quantum state of lower energy. In the process, a photon is emitted with the same characteristics as the incident photon.
  - (iii) In *spontaneous emission*, a system emits a photon and makes a transition from a quantum state of higher energy to a quantum state of lower energy, irrespective of any incident radiation.
- (b) The term  $B_{12}u(\omega_{21})N_1$  corresponds to the rate of transfer of atoms from quantum state 1 to quantum state 2 due to absorption.

The term  $B_{21}u(\omega_{21})N_2$  corresponds to the rate of transfer of atoms from quantum state 2 to quantum state 1 due to stimulated emission.

The term  $A_{21}N_2$  corresponds to the rate of transfer of atoms from quantum state 2 to quantum state 1 due to spontaneous emission.

**Comments** (1) Note that the first index in  $B_{12}$ ,  $B_{21}$  and  $A_{21}$  refers to the initial state and the second index refers to the final state.

(2) Using the Boltzmann distribution law and the Planck distribution law, we can show that the two  $B$ -coefficients are equal to one and obtain an expression for the  $A$ -coefficient in terms of the  $B$ -coefficients. The  $B$ -coefficients are found from first-order time-dependent perturbation theory, and the  $A$ -coefficient found from them. This gives us an indirect way of predicting the rate of spontaneous transitions from an upper quantum state to a lower quantum state.